

**Appendix E**  
**Drag-Out Model**

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## Estimates of Drag-out, Wastewater and Surface Water Concentrations

Process Name: Non-conveyorized HASL  
 Production Rate, sq.m./d: 553  
 Number of Process Tanks: 2  
 Plant WW Flowrate, L/d: 27911  
 Stream Flow rate, L/d: 13,300,000

### Summary of all Chemicals in Process Wastewater

Chemical Name	Drag-out, g/d	Bath Replacement, g/d	Total in Wastewater, g/d	Concentration in Wastewater, mg/L	Stream Concentration w/o Treatment, mg/L <sup>a</sup>	Treatment Efficiency, %	Stream Concentration Following POTW Treatment, mg/L
1,4-Butenediol	861	507	1368	49	<b>0.10</b>	90	0.010
Alkylakyne diol	8.4	4.7	13	0.47	0.00098		
Alkylaryl sulfonate	42	23	65	2.3	<b>0.0049</b>	0	0.0049
Alkylphenol ethoxylate	106	59	165	5.9	0.012		
Alkylphenolpolyethoxyethanol	999	558	1557	56	0.12		
Aryl phenol	2.9	1.7	4.6	0.16	0.00034		
Citric acid	1679	937	2616	94	<b>0.20</b>	93	0.014
Copper sulfate pentahydrate	3046	1792	4838	173	<b>0.36</b>	86	0.051
Ethoxylated alkylphenol	144	80	224	*	0.02		
Ethylene glycol	3087	1731	4818	173	0.36		
Ethylene glycol monobutyl ether	1271	709	1980	71	<b>0.15</b>	90	0.015
Fluoboric acid	684	382	1066	38	0.080		
Gum	12	6.8	18	0.66	0.0014		
Hydrochloric acid	1157	646	1802	65	0.14		
Hydrogen peroxide	3434	2021	5454	195	<b>0.41</b>	90	0.041
Hydroxyaryl acid	16	10	26	0.92	0.0019		
Hydroxyaryl sulfonate	28	17	45	1.6	0.0034		
Phosphoric acid	3391	1893	5285	189	0.40		
Potassium peroxymonosulfate	6883	4051	10934	392	<b>0.82</b>	90	0.082
Sodium benzene sulfonate	8.3	4.6	13	0.46	0.00097		
Sodium hydroxide	12	6.8	18	0.65	0.0014		
Sulfuric acid	13132	7543	20675	741	1.6		

<sup>a</sup> Numbers in bold indicate the estimated stream concentration (without wastewater treatment) that exceeds the aquatic toxicity concern concentration.

## Estimates of Wastewater and Surface Water Concentrations

Process Name: Conveyorized HASL  
 Production Rate, sq.m./d: 1108  
 Number of Process Tanks: 2  
 Plant WW Flowrate, L/d: 44829  
 Stream Flow rate, L/d: 13,300,000

### Summary of all Chemicals in Process Wastewater

Chemical Name	Bath Replacement, g/d	Concentration in Wastewater, mg/L	Stream Concentration w/o Treatment, mg/L <sup>a</sup>	Treatment Efficiency, %	Stream Concentration Following POTW Treatment, mg/L
1,4-Butenediol	1016	23	<b>0.076</b>	90	0.0076
Alkylakyne diol	9.4	0.21	0.00070		
Alkylaryl sulfonate	47	1.0	<b>0.0035</b>	0	0.0035
Alkylphenol ethoxylate	119	2.6	0.0089		
Alkylphenolpolyethoxyethanol	1118	25	0.084		
Aryl phenol	3.4	0.076	0.00025		
Citric acid	1879	42	<b>0.14</b>	93	0.0099
Copper sulfate pentahydrate	3593	80	<b>0.27</b>	86	0.038
Ethoxylated alkyphenol	161	3.6	0.0121		
Ethylene glycol	3470	77	0.26		
Ethylene glycol monobutyl ether	1422	32	<b>0.11</b>	90	0.011
Fluoboric acid	766	17	0.057		
Gum	14	0.30	0.0010		
Hydrochloric acid	1294	29	0.097		
Hydrogen peroxide	4050	90	<b>0.30</b>	90	0.030
Hydroxyaryl acid	19	0.43	0.0014		
Hydroxyaryl sulfonate	33	0.75	0.0025		
Phosphoric acid	3795	85	0.28		
Potassium peroxymonosulfate	8120	181	<b>0.61</b>	90	0.061
Sodium benzene sulfonate	9.3	0.21	0.00070		
Sodium hydroxide	14	0.30	0.0010		
Sulfuric acid	15120	337	1.1		

<sup>a</sup> Numbers in bold indicate the estimated stream concentration (without wastewater treatment) that exceeds the aquatic toxicity concern concentration.

### Estimates of Drag-out, Wastewater and Surface Water Concentrations

Process Name: Non-conveyorized Nickel/Gold  
 Production Rate, sq.m./d: 113.9  
 Number of Process Tanks: 6  
 Plant WW Flowrate, L/d: 9595  
 Stream Flow rate, L/d: 13,300,000

### Summary of all Chemicals in Process Wastewater

Chemical Name	Drag-out, g/d	Bath Replacement, g/d	Total in Wastewater, g/d	Concentration in Wastewater, mg/L	Stream Concentration w/o Treatment, mg/L <sup>a</sup>	Treatment Efficiency, %	Stream Concentration Following POTW Treatment, mg/L
Aliphatic acid A	136	82	219	23	0.016		
Aliphatic acid B	20	12	32	3.4	0.0024		
Aliphatic acid E	306	184	491	51	0.037		
Aliphatic dicarboxylic acid A	96	58	154	16	0.012		
Aliphatic dicarboxylic acid C	45	27	73	7.6	0.0055		
Alkylamino acid B	337	45	383	40	0.029		
Alkyl diol	581	93	673	70	0.051		
Alkylphenolpolyethoxyethanol	206	33	239	25	0.018		
Ammonia compound B	1.0	0.57	1.5	0.16	0.00011		
Ammonium chloride	745	100	845	88	0.064		
Ammonium hydroxide	480	65	545	57	0.041		
Citric acid	134	16	150	16	0.011		
Copper sulfate pentahydrate	627	123	750	78	<b>0.056</b>	86	0.0079
Ethoxylated alkylphenol	12	2.0	14	1.5	0.0011		
Hydrochloric acid	7601	569	8170	851	0.61		
Hydrogen peroxide	500	98	598	62	<b>0.045</b>	90	0.0045
Hydroxyaryl acid	3.3	0.66	4.0	0.42	0.00030		
Inorganic metallic salt A	0.029	0.017	0.046	0.0048	0.0000035		
Inorganic metallic salt B	1.9	1.1	3.1	0.32	0.00023		
Inorganic metallic salt C	0.020	0.012	0.032	0.0033	0.0000024		
Malic acid	205	123	328	34	0.025		
Nickel sulfate	508	306	814	85	<b>0.061</b>	24	0.051
Palladium chloride	18	2.4	20	2.1	0.0015		
Phosphoric acid	581	93	673	70	0.051		
Potassium compound	959	577	1535	160	0.12		
Potassium gold cyanide	41	5.5	46	4.8	<b>0.0035</b>	66	0.0045
Sodium hydroxide	2.4	0.47	2.8	0.30	0.00021		
Sodium hypophosphite mono hydrate	585	352	936	98	0.070		
Sodium salt	1229	164	1393	145	0.10		
Substituted amine hydroxhloride	818	109	928	97	<b>0.070</b>	80	0.014
Sulfuric acid	2796	491	3287	343	0.25		
Transition metal salt	8.2	1.1	9.3	1.0	0.00070		
Urea compound B	0.7	0.4	1.1	0.1	0.00008		

<sup>a</sup> Numbers in bold indicate the estimated stream concentration (without wastewater treatment) that exceeds the aquatic toxicity concern concentration.

### Estimates of Drag-out, Wastewater and Surface Water Concentrations

Process Name: Non-conveyorized Nickel/Palladium/Gold  
 Production Rate, sq.m./d: 86  
 Number of Process Tanks: 8  
 Plant WW Flowrate, L/d: 12703  
 Stream Flow rate, L/d: 13,300,000

### Summary of all Chemicals in Process Wastewater

Chemical Name	Drag-out, g/d	Bath Replacement, g/d	Total in Wastewater, g/d	Concentration in Wastewater, mg/L	Stream Concentration w/o Treatment, mg/L <sup>a</sup>	Treatment Efficiency, %	Stream Concentration Following POTW Treatment, mg/L
Aliphatic acid B	15	9.2	24	1.9	0.0018		
Aliphatic acid E	308	186	494	39	0.037		
Aliphatic dicarboxylic acid A	72	44	116	9.1	0.0087		
Aliphatic dicarboxylic acid C	34	21	55	4.3	0.0041		
Alkylamino acid B	451	61	512	40	0.038		
Alkyldiol	438	70	509	40	0.038		
Alkylpolyol	389	892	1282	101	0.096		
Amino acid salt	21	1.4	22	1.7	0.0017		
Amino carboxylic acid	10	23	34	2.7	0.0025		
Ammonia compound A	513	69	582	46	0.044		
Ammonia compound B	0.72	0.44	1.2	0.091	0.000087		
Ammonium hydroxide	615	83	698	55	0.052		
Citric acid	124	15	139	11	0.010		
Copper sulfate pentahydrate	474	93	567	45	<b>0.043</b>	86	0.0060
Ethoxylated alkylphenol	9.3	1.5	11	0.85	0.00081		
Ethylenediamine	46	105	150	12	0.011		
Hydrochloric acid	1268	159	1427	112	0.11		
Hydrogen peroxide	378	74	452	36	<b>0.034</b>	90	0.0034
Hydroxyaryl acid	2.5	0.50	3.0	0.24	0.00023		
Inorganic metallic salt B	6.6	13	19	1.5	<b>0.0015</b>	82	0.00026
Maleic acid	20	47	67	5.3	0.0051		
Malic acid	155	93	248	20	0.019		
Nickel sulfate	604	365	969	76	<b>0.073</b>	24	0.055
Palladium salt	33	74	107	8.4	0.0080		
Phosphoric acid	438	70	509	40	0.038		
Potassium compound	724	437	1160	91	0.087		
Potassium gold cyanide	31	4.1	35	2.7	0.0026		
Propionic acid	75	171	246	19	0.018		
Sodium hydroxide	1.8	0.35	2.1	0.17	0.00016		
Sodium hypophosphite mono hydrate	625	463	1088	86	0.082		
Sodium salt	1548	166	1714	135	0.13		
Substituted amine hydrochloride	618	83	701	55	<b>0.053</b>	80	0.011
Sulfuric acid	1646	324	1970	155	0.15		
Surfactant	1.0	2.3	3.4	0.27	0.00025		
Transition metal salt	6.2	0.83	7.0	0.55	0.00053		
Urea compound B	1.0	0.62	1.7	0.13	0.00120		

<sup>a</sup> Numbers in bold indicate the estimated stream concentration (without wastewater treatment) that exceeds the aquatic concern concentration.

Process Name: Non-Conveyorized OSP  
 Production Rate, sq.m./d: 686  
 Number of Process Tanks: 3  
 Plant WW Flowrate, L/d: 21631  
 Stream Flow rate, L/d: 13,300,000

**Summary of all Chemicals in Process Wastewater**

Chemical Name	Drag-out, g/d	Bath Replacement, g/d	Total in Wastewater, g/d	Concentration in Wastewater, mg/L	Stream Concentration w/o Treatment, mg/L <sup>a</sup>	Treatment Efficiency, %	Stream Concentration Following POTW Treatment, mg/L
Acetic acid	4951	339	5289	245	0.40		
Alkylaryl imidazole	4054	277	4332	200	<b>0.33</b>	90	0.033
Aromatic imidazole product <sup>b</sup>	519	35	554	26	0.042		
Arylphenol	3.6	2.1	5.7	0.26	0.00430		
Copper ion	4054	277	4332	200	<b>0.33</b>	86	0.046
Copper salt C	112	8	119	5.5	<b>0.0089</b>	86	0.00130
Copper sulfate pentahydrate	3778	2225	6003	278	<b>0.45</b>	86	0.063
Ethoxylated alkylphenol	74	42	116	5.4	0.0087		
Ethylene glycol	3829	2149	5978	276	0.45		
Gum	14	8	23	1.1	0.0017		
Hydrochloric acid	1639	916	2555	118	0.19		
Hydrogen peroxide	1525	898	2423	112	<b>0.18</b>	90	0.018
Hydroxyaryl acid	20	12	32	1.50	0.0024		
Hydroxyaryl sulfonate	35	21	56	2.6	0.0042		
Phosphoric acid	3497	1954	5451	252	0.41		
Sodium hydroxide	14	8	23	1.10	0.0017		
Sulfuric acid	21683	12751	34433	1592	2.6		

<sup>a</sup> Numbers in bold indicate the estimated stream concentration (without wastewater treatment) that exceeds the aquatic toxicity concern concentration.

<sup>b</sup> This ingredient not evaluated further as there was not enough information provided to identify a specific chemical.

Process Name: Conveyorized OSP  
 Production Rate, sq.m./d: 1500  
 Number of Process Tanks: 3  
 Plant WW Flowrate, L/d: 32232  
 Stream Flow rate, L/d: 13,300,000

**Summary of all Chemicals in Process Wastewater**

Chemical Name	Bath Replacement, g/d	Concentration in Wastewater, mg/L	Stream Concentration w/o Treatment, mg/L <sup>a</sup>	Treatment Efficiency, %	Stream Concentration Following POTW Treatment, mg/L
Acetic acid	2963	92	0.22		
Alkylaryl imidazole	2427	75	<b>0.18</b>	90	0.018
Aromatic imidazole product <sup>b</sup>	310	10	0.023		
Arylphenol	4.6	0.14	0.00034		
Copper ion	2427	75	<b>0.18</b>	86	0.025
Copper salt C	67	2.1	<b>0.0050</b>	86	0.00070
Copper sulfate pentahydrate	4865	151	<b>0.36</b>	86	0.051
Ethoxylated alkyphenol	91	2.8	0.0068		
Ethylene glycol	4699	146	0.35		
Gum	18	0.6	0.0014		
Hydrochloric acid	2002	62	0.15		
Hydrogen peroxide	1964	61	<b>0.15</b>	90	0.015
Hydroxyaryl acid	26	0.81	0.0019		
Hydroxyaryl sulfonate	45	1.4	0.0034		
Phosphoric acid	4272	133	0.32		
Sodium hydroxide	18	0.57	0.0014		
Sulfuric acid	27877	865	2.1		

<sup>a</sup> Numbers in bold indicate the estimated stream concentration (without wastewater treatment) that exceeds the aquatic toxicity concern concentration.

<sup>b</sup> This ingredient not evaluated further as there was not enough information provided to identify a specific chemical.

## Estimates of Wastewater and Surface Water Concentrations

Process Name: Conveyorized Immersion Silver  
 Production Rate, sq.m./d: 376  
 Number of Process Tanks 4  
 Plant WW Flowrate, L/d 8083  
 Stream Flow rate, L/d: 13,300,000

### Summary of all Chemicals in Process Wastewater

Chemical Name	Bath Replacement, g/d	Concentration in Wastewater, mg/L	Stream Concentration w/o Treatment, mg/L <sup>a</sup>	Treatment Efficiency, %	Stream Concentration Following POTW Treatment, mg/L
1,4-Butenediol	390	48	<b>0.029</b>	90	0.0029
Alkylamino acid A	1603	198	0.12		
Fatty amine	62	7.7	<b>0.0047</b>	95	0.00023
Hydrogen Peroxide	3462	428	<b>0.26</b>	90	0.026
Nitrogen acid	281	35	0.021		
Nonionic Surfactant <sup>b</sup>	345	43	0.026		
Phosphoric acid	2891	358	0.22		
Silver Nitrate	8.4	1.0	<b>0.00063</b>	96	0.000025
Sodium hydroxide	621	77	0.047		
Sulfuric acid	141	17	0.011		

<sup>a</sup> Numbers in bold indicate the estimated stream concentration (without wastewater treatment) that exceeds the aquatic toxicity concern concentration.

<sup>b</sup> This ingredient not evaluated further as there was not enough information provided to identify a specific chemical.

## Estimates of Drag-out, Wastewater and Surface Water Concentrations

Process Name: Non-conveyorized Immersion Tin  
 Production Rate, sq.m./d: 321  
 Number of Process Tanks: 4  
 Plant WW Flowrate, L/d: 23624  
 Stream Flow rate, L/d: 13,300,000

### Summary of all Chemicals in Process Wastewater

Chemical Name	Drag-out, g/d	Bath Replacement, g/d	Total in Wastewater, g/d	Concentration in Wastewater, mg/L	Concentration in Stream, mg/L <sup>a</sup>	Treatment Efficiency, %	Concentration in Stream following POTW Treatment, mg/L
Aliphatic acid D	493	33	526	22	0.039		
Alkylalkyne diol	4.9	0.78	5.7	0.24	0.00042		
Alkylamino acid B	779	51	830	35	0.062		
Alkylaryl sulfonate	24	3.9	28	1.2	<b>0.0021</b>	0	0.0021
Alkylimine dialkanol	26	1.7	28	1.2	0.0021		
Alkylphenol ethoxylate	61	9.8	71	3.0	0.0054		
Bismuth compound	1.0	0.066	1.1	0.045	0.000080		
Citric acid	14599	1056	15655	663	<b>1.2</b>	93	0.082
Cyclic amide	1983	131	2115	90	0.16		
Ethoxylated alkylphenol	49	7.8	57	2.4	0.0042		
Ethylene glycol monobutyl ether	738	118	856	36	<b>0.064</b>	90	0.0064
Fluoboric acid	397	63	461	19	0.035		
Hydrochloric acid	279	18	298	13	0.022		
Hydroxy carboxylic acid	1633	108	1741	74	0.13		
Methane sulfonic acid	15636	1046	16682	706	1.3		
Phosphoric acid	974	156	1130	48	0.085		
Potassium peroxymonosulfate	3996	785	4780	202	<b>0.36</b>	90	0.036
Quantenary alkylammonium chlorides	922	61	983	42	<b>0.074</b>	90	0.0074
Silver salt	0.15	0.010	0.16	0.0067	0.000012		
Sodium benzene sulfonate	4.8	0.77	5.6	0.24	0.00042		
Sodium phosphorus salt	3475	231	3706	157	0.28		
Stannous methane sulfonic acid	4352	288	4640	196	<b>0.35</b>	40	0.21
Sulfuric acid	10239	1325	11564	490	0.87		
Thiourea	3799	251	4050	171	<b>0.30</b>	90	0.030
Tin chloride	544	36	580	25	<b>0.044</b>	40	0.026
Unspecified tartrate	973	64	1037	44	0.078		
Urea	3503	231	3735	158	0.28		
Urea compound C	779	51	830	35	<b>0.062</b>	90	0.0062
Vinyl polymer	493	33	526	22	0.039		

<sup>a</sup> Numbers in bold indicate the estimated stream concentration (without wastewater treatment) that exceeds the aquatic toxicity concern concentration.

## Estimates of Wastewater and Surface Water Concentrations

Process Name: Conveyorized Immersion Tin  
 Production Rate, sq.m./d: 226  
 Number of Process Tanks: 4  
 Plant WW Flowrate, L/d: 8106  
 Stream Flow rate, L/d: 13,300,000

### Summary of all Chemicals in Process Wastewater

Chemical Name	Bath Replacement, g/d	Concentration in Wastewater, mg/L	Stream Concentration w/o Treatment, mg/L <sup>a</sup>	Treatment Efficiency, %	Stream Concentration Following POTW Treatment, mg/L
Aliphatic acid D	23	2.8	0.0017		
Alkylalkyne diol	0.55	0.067	0.000041		
Alkylamino acid B	36	4.5	0.0027		
Alkylaryl sulfonate	2.7	0.34	0.00021		
Alkylimine dialkanol	1.2	0.15	0.000092		
Alkylphenol ethoxylate	6.9	0.85	0.00052		
Bismuth compound	0.046	0.0057	0.0000035		
Citric acid	742	92	0.056		
Cyclic amide	92	11	0.0069		
Ethoxylated alkylphenol	5.5	0.67	0.00041		
Ethylene glycol monobutyl ether	83	10	0.0062		
Fluoboric acid	45	5.5	0.0033		
Hydrochloric acid	13	1.6	0.0010		
Hydroxy carboxylic acid	76	9.4	0.0057		
Methane sulfonic acid	735	91	0.055		
Phosphoric acid	109	13	0.0082		
Potassium peroxymonosulfate	551	68	<b>0.041</b>	90	0.0041
Quantenary alkylammonium chlorides	43	5.3	0.0032		
Silver salt	0.0069	0.00086	0.00000052		
Sodium benzene sulfonate	0.54	0.067	0.000041		
Sodium phosphorus salt	163	20	0.012		
Stannous methane sulfonic acid	202	25	0.015		
Sulfuric acid	932	115	0.070		
Thiourea	176	22	0.013		
Tin chloride	25	3.1	0.0019		
Unspecified tartrate	45	5.6	0.0034		
Urea	163	20	0.012		
Urea compound C	36	4.5	0.0027		
Vinyl polymer	23	2.8	0.0017		

Numbers in bold indicate the estimated stream concentration (without wastewater treatment) that exceeds the aquatic toxicity concern concentration.

**PREDICTION OF WATER QUALITY  
FROM PRINTED WIRING BOARD PROCESSES**

**Final Report to the University of Tennessee Center for Clean Products and  
Clean Technologies and to the U.S. Environmental Protection Agency**

**Part of the Verification of Finishing Technologies Project  
EPA Grant X825373-01-2 (Amendment No. 2)**

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## INTRODUCTION

The Design for the Environment (DFE) Project Printed Wiring Boards (PWB) Cleaner Technologies Substitutes Assessment: Making Holes Conductive (MHC) was performed by the Center for Clean Products and Clean Technologies (CCPCT) at the University of Tennessee. The project and results were well received by industry and the U.S. Environmental Protection Agency. However, all parties agreed that one weakness in the project was the evaluation of impacts of chemicals in the wastewater discharges of bath solutions from the MHC plating lines. Evaluation of these impacts was more difficult than anticipated partly because of insufficient information from surveyed facilities on the water quality of their discharges. Attempts at a mass balance to predict chemical discharges were also unsatisfactory due to insufficient data on chemical use and ultimate fate.

An estimate of the pollutants in the raw wastewater from PWB plating processes is needed in order to evaluate health risks, impacts on the environment, impacts on municipal wastewater plants, and overall manufacturing costs which includes treatment/disposal costs. The main source of pollutants in the raw wastewater is the drag-out from the baths. Hence, drag-out is the key variable for determining pollutant mass.

PWB facilities analyze at most only a couple of chemicals in their wastewater, and the facilities generally have insufficient data to calculate chemical mass balances. Therefore, a different approach is required to estimate the pollutant loads and wastewater quality of the PWB wastewater discharges. This report discusses the development, validation, and use of predictive tools to satisfy this need.

### **Objectives:**

The objectives of this research were:

- Develop tools and methodologies to predict, but more importantly to compare the mass of pollutants in the raw wastewater discharges from PWB plating processes.
- Validate these tools and methodologies against data available in the literature and against samples collected at PWB facilities.

## LITERATURE REVIEW

Literature was identified through a computerized search on several key words. Additional papers were found from the references in papers and from a manual search of recent *Chemical Abstracts* (1998).

### Pollutant Generation Rate and Waste Generation Volume

The sources of the pollutants in the wastewater generated in the MHC and surface finishing processes for PWB manufacturing are the chemicals that escape from the process baths and from other processes such as stripping racks of plating deposits. Our assumption for estimating the pollutant mass generation rate, e.g., kg Cu/day, is that the source of the pollutants is predominantly the drag-out from the process baths. Whatever chemicals are drug out of the process tanks by solution adhering to the surface of the boards and racks will be removed in the rinse tanks and ultimately end up in the raw wastewater discharge before any treatment or metals recovery. This is consistent with the literature (Mooney 1991) and is expressed in a simple mass balance:

$$\left( \begin{array}{c} \text{mass of pollutants} \\ \text{in drag - out} \end{array} \right) = \left( \begin{array}{c} \text{mass of pollutants} \\ \text{in rinse discharge} \end{array} \right) \quad \text{Eqn 1}$$

As discussed later, the etchant process baths themselves are generally not dumped into the wastewater at the end of their useful life, but are typically sent off-site for processing. Other process baths are apparently not sent off-site and do need to be accounted for in the waste generation. Although pollutants from the stripping of racks may be significant at times, the average mass pollutants originating from this process should be less than that contributed by drag-out. Therefore, an estimate of the expected drag-out from various process tanks under differing conditions is critical for estimating the waste mass generation rate. The arrangement of the rinse tanks and the rinse flow rates will not change the total mass of contaminants released, only the concentration and the volume of wastes. The waste generation volume primarily depends on the rinse flow rates since this is the main source of wastewater discharge. If certain assumptions are made, then conventional rinsing theory may be used to estimate the volume of waste based on the drag-out and needed final rinse water quality. Importantly, the primary goal of this work is a methodology that can be used to compare the relative amounts of wastes generated from alternative PWB surface finishing manufacturing processes.

There are many references giving advice on minimizing drag-out and rinse water. Factors that will reduce the drag-out include slow withdrawal from the process tank, longer drainage times, tilting the boards so that the liquid drains to a corner, using drip shields, using drag-out/drag-in tanks, as well as others. Solution density, viscosity, which depends on the bath chemistry and temperature, and surface tension also affect how well the liquid drains off the boards, and hence affects drag-out. Because of the number of variables which have complex relationships with drag-out, estimating drag-out for a series of baths is a difficult, unsolved problem. The following sections review what is known about estimating drag-out, including several references that include predictive equations and experimental measurements.

## **Drag-Out Tests at Micom, Inc.**

The MnTAP/EPA Write study (Pagel 1992) at Micom, Inc. evaluated the ability of two modifications to reduce waste from PWB surface finishing processes. At the time of the study, Micom produced 92 - 111 m<sup>2</sup>/day of double-sided and multilayered PWBs with the average board being 0.46 m by 0.53 m and having 8000 holes. Micom had already implemented several waste reduction measures, including countercurrent rinses, flow restrictors, softened water in the rinses (softened water improved the rinsing and increased the efficiency of the ion exchange waste treatment system), and air and mechanical agitation. However, Micom evaluated whether changes to the way PWBs were transferred from process baths to the rinse tanks could further reduce the amount of waste by reducing the drag-out.

Two processes were tested at Micom, Inc. in their MHC line: 1) a micro-etch bath and the countercurrent rinse tanks following it; and 2) an electroless copper bath and the countercurrent rinse tanks following it. The PWBs were moved from tank to tank in racks. The racks were 0.86 m high by 0.50 m wide by 0.33 m deep and could hold 24 boards. Typically, the operator controlled a hoist and allowed the rack to drain for 3-5 seconds before going into the next tank. The residence time was about 75 seconds in the micro-etch tank, 30 minutes in the electroless copper tank, which held two racks at a time, and 2-3 minutes in each rinse tank.

The modifications evaluated at Micom were: 1) slowing the withdrawal rate of the racks from the process bath; and 2) using an intermediate rack withdrawal rate combined with a longer drain time over the process bath before going into the rinse tanks. Slowing the withdrawal rate was achieved by lowering the speed of the motor on the mechanical hoist used to move the racks. Installation of new equipment prohibited matching the withdrawal rates used in the first modification with tests on the second modification, hence the designation of "intermediate" withdrawal rate. Withdrawal time was defined as the time it took to raise the boards from the bath to a height needed to clear the tank walls, a total of 0.91 m. Increasing the drain time was achieved by the operator simply waiting longer before placing the boards in the next bath. Drain time was defined from the moment that the rack cleared the water surface until half of the rack was over the adjacent rinse tank. Measurement of drag-out was accomplished by shutting off the rinse water and then measuring the increase in copper concentration after a known quantity of boards had been rinsed. Copper was measured by atomic absorption spectrophotometry. The electroless copper samples were preserved with a hydrochloric/nitric acid mixture rather than just nitric, because copper precipitated out of solution as the solution cooled when nitric acid alone was used. There were some analytical difficulties of unknown origin in that the copper measurements done by an outside laboratory showed about 1800-2200 mg/L of copper whereas Micom's laboratory analyses showed about 2400 mg/L.

Baseline drag-out measurements were made over a twelve day period using 136 samples for 12 pairs of racks. The first modification experiments were also made using 136 samples for 12 pairs of racks, and the second modification experiments used 109 samples for 9 pairs of racks.

The results of the experiments are summarized in Tables 1 and 2. It should be noted that the values for drag-out, withdraw rate, and drain time are averages of a rather broad range of values grouped by relative magnitude by Page 1.

**Table 1. Drag-Out Test Results on the Microetch Bath at Micom, Inc.**

Parameter	Baseline	Slow Withdrawal Rate	Intermediate Withdrawal Rate & Longer Drain Time
Drag-out, mL/m <sup>2</sup>	129	72.1	76.4
Withdrawal time, sec	1.7	14.9	4.3
Withdrawal rate, m/sec	0.51	0.056	0.20
Drain time, sec	3.4	2.5	12.1
Total time, sec	5.1	17.4	16.4
Surface area/rack, m <sup>2</sup>	8.2	7.7	8.6
Water flow rate, lpm	9.8	---	---

**Table 2. Drag-Out Test Results on the Electroless Bath at Micom, Inc.**

Parameter	Baseline	Slow Withdrawal Rate	Intermediate Withdrawal Rate & Longer Drain Time
Drag-out, mL/m <sup>2</sup>	64.6	32.3	31.4
Withdrawal time, sec	1.8	13.9	4.3
Withdrawal rate, m/min	0.48	0.061	0.175
Drain time, sec	5.2	3.2	11.9
Total time, sec	7.0	17.1	16.3
Surface area/rack, m <sup>2</sup>	15.7	15.0	16.3
Water flow rate, lpm	12.5	---	—

For the micro-etch bath, the first modification reduced the drag-out by 45% while the second modification reduced drag-out by 41%. For the electroless copper bath, the reductions were 50% and 52%, respectively. Because it was easier for Micom to control the drain time than the withdrawal rate, they implemented a longer drain time.

It should be noted that reducing the drag-out from the micro-etch affects the bath. This bath removes copper until the etchants are exhausted. Make-up chemicals may be added to replace etchant solution is lost in drag-out. Reducing drag-out may mean that the entire bath must be replaced more frequently, because of increased copper build-up in the bath. However, Micom preferred to retain the copper in the bath and replace the bath, because there is greater opportunity to recover metals in the etchant bath than in the rinses. For the electroless bath, drag-out reduction helps retain the chemicals in the bath and increase its life, providing that build-up of impurities does not offset this advantage. Reduction of drag-out from upstream baths would help in this regard.

### Other Published Drag-Out Estimates

Süß (1990) evaluated several ways to minimize drag-out, including the effect of the inclination angle during drainage, the withdrawal rate, and the drainage time. Several experiments focused on the inclination angle in the design of electroplating product holders and its effect on drag-out. The holders were not for PWBs but apparently for a variety of electroplated products. The holders typically had horizontal cross-braces or struts. Süß noted that the drag-out from the holder could be as much as 50% of the total drag-out in these cases. Süß experimented with holder designs that had struts of different angles and showed that drag-out could be reduced significantly. The effect of the inclination angle of the struts on drag-out is shown in Table 3. Struts tilted at a 45° angle to horizontal had only 36% of the drag-out as a horizontal one.

**Table 3. Effect of Inclination Angle of the Product Holder Strut on Drag-Out**

Angle to Horizontal	Drag-Out mL/m <sup>2</sup>	% of Maximum
0°	44	100
15°	35	80
30°	25	57
45°	16	36
90°	22	50

Süß (1990) also experimented with chromium plated sheets suspended from the holders to determine the effect of drainage time and inclination angle of the sheet. The experiments used either 19-20 g/L or 240-250 g/L CrO<sub>3</sub> electrolytes. The effect of drainage time and inclination angle is shown in Table 4. (Note: the data reported in Table 4 were read from two graphs in Süß (1990) and include representative data, but not all the data.). As seen in the table, a 45° inclination angle had about 33% less drag-out at short drainage times compared to a horizontal angle and nearly 50% less drag-out at long drainage times. An increase in the drainage time greatly reduced drag-out up to about 20-30 seconds, but had a relatively small effect for longer times. Further experiments were conducted on the effect of withdrawal rate and inclination angle of the sheet. The effect of withdrawal rate is shown in Table 5. Slower withdrawal rates reduced the drag-out, but not as much as inclination angle. A plate withdrawn at 60 m/min had roughly 25-30% more drag-out volume than a plate withdrawn at 6 m/min. The drag-out volumes reported by Süß are approximately a factor of two less than the drag-out volumes reported in the Micom study (Pagel 1992) discussed above. One explanation for the difference may be that the boards in the Süß study did not contain holes but the boards used in the Micom study did. It should be noted that Süß was not clear how the drag-out was calculated. It appears to be American practice to report the drag-out in terms of the area of one side of the board. It is possible that Süß calculated his drag-out based on the area of both sides of the board, leading to numbers which are half as large. If this were the case, then to be comparable to American practice, his drag-out volumes should be doubled. However, in a later paper, Süß (1992) used an equation which was developed for drag-out on the basis of one side of the board. It is likely that he was aware of the assumptions built into the equation, and considering that his values are comparable to the Micom study, we will assume that Süß's drag-out volumes are directly comparable to other values. In either case, the trends are the same.

**Table 4. Effect of Drainage Time and Inclination Angle on Drag-Out.**

Drainage Time, s	Drag-Out, mL/m <sup>2</sup>			
	280-320 g/L CrO <sub>3</sub> , 0° angle, 40°C	280-320 g/L CrO <sub>3</sub> , 45° angle, 40°C	20 g/L CrO <sub>3</sub> , 0° angle, 20°C	20 g/L CrO <sub>3</sub> , 45° angle, 20°C
0	57	--	64	--
10	28	21	33	24
20	22	13	28	19
30	20	11	25	15
45	19	--	21	13
60	19	10	19	11

**Table 5. Effect of Withdrawal Rate on Drag-Out.**

Withdrawal Rate, m/min	Drag-Out	
	240-250 g/L CrO <sub>3</sub> , (40±1°C)	19-20 g/L CrO <sub>3</sub> , (20±1°C)
	mL/m <sup>2</sup>	mL/m <sup>2</sup>
3.6	17	21
6	22	26
9	24.5	29
18	26.5	32
36	27	33
60	28	33

In a second paper, Süß (1992) evaluated two drag-out prediction equations by comparing measured volumes of drag-out to predicted values. The first equation was from Kushner (1951):

$$f = 0.02 \sqrt{\frac{m \cdot h}{r \cdot t_w}} \quad \text{Eqn 2}$$

or:

$$f = 0.02\sqrt{n \cdot v_A} \quad \text{Eqn 3}$$

where:

- f = film thickness, cm
- $\mu$  = dynamic viscosity of electrolyte, g/(cm·s)
- h = height of metal sheet
- $\rho$  = density of electrolyte, gm/cm<sup>3</sup>
- t<sub>w</sub> = withdrawal time, s
- v = kinematic viscosity, cm<sup>2</sup>/s
- v<sub>A</sub> = withdrawal rate of metal sheet, cm/s

The second equation was:

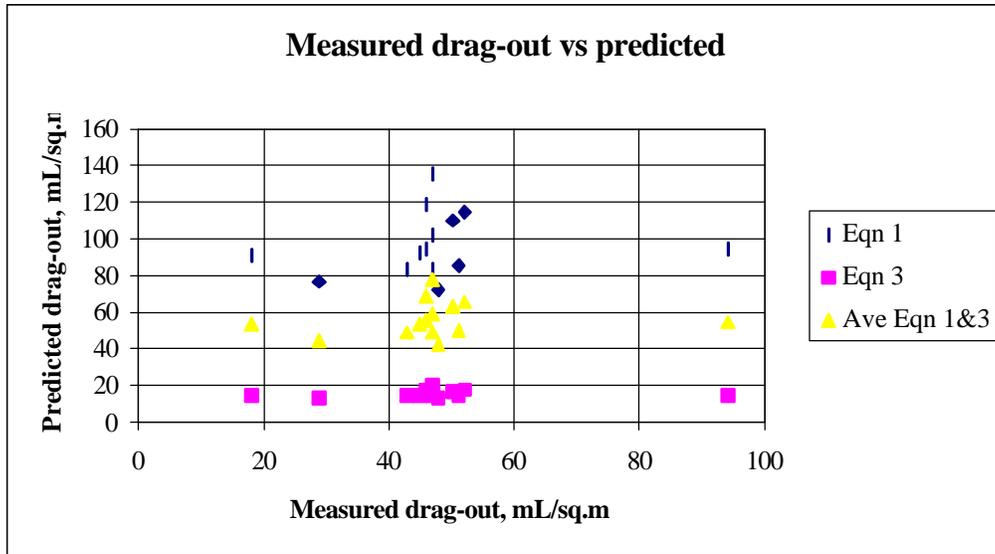
$$f = \sqrt{\frac{2n \cdot h \cdot v_A}{9g(h + 4v_A t_{dr})}} \quad \text{Eqn 4}$$

where:

- g = gravity, 981 cm/s<sup>2</sup>
- t<sub>dr</sub> = drainage time, s

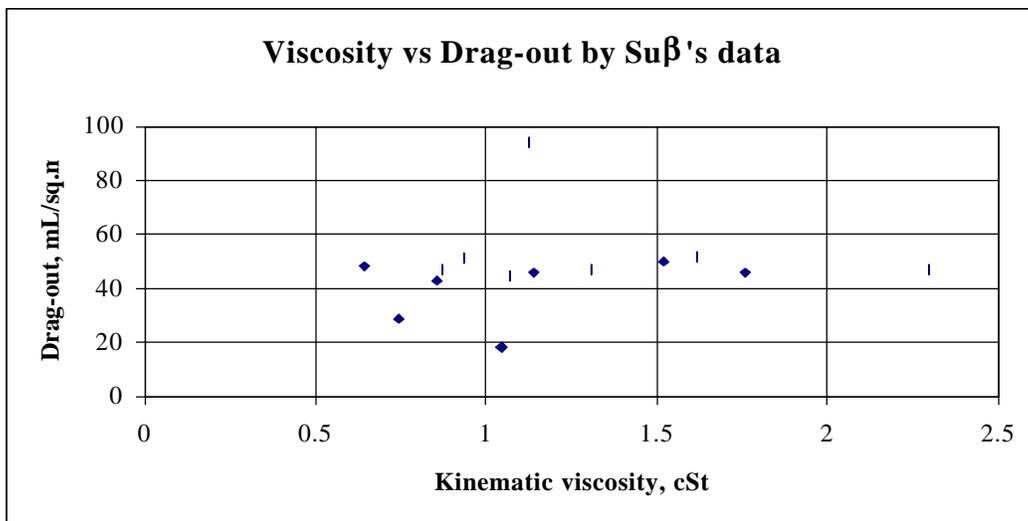
Experiments were conducted on 21.0 x 21.4 cm metal sheets which had no holes. The sheets were withdrawn from the bath at 20 cm/s and allowed to drain for 10 seconds.

Neither of the two equations predicted the measured values very well. Sixteen different electrolytes were tested with concentrations ranging from 17 to 300 gm/L of material, densities ranging from 1.015 to 1.562 g/cm<sup>3</sup>, dynamic viscosities ranging from 0.713 to 8.6 cP, and temperatures ranging from 18 to 59.5°C. The average measured drag-out was 47.4 mL/m<sup>2</sup> with a standard deviation of 16.3 mL/m<sup>2</sup>. The average predicted drag-out and standard deviation predicted by equation 3 were 96.8 and 17.8 mL/m<sup>2</sup>, respectively, while equation 4 had average predicted drag-out and standard deviation of 15.6 and 2.06 mL/m<sup>2</sup>, respectively. A linear regression of measured versus predicted drag-out volumes gave an r<sup>2</sup> of 0.021 and 0.012 for equations 3 and 4, respectively. Taking an average of the two equations yielded no better results. A scatter plot of the measured drag-out and the predicted drag-out is shown in Figure 1.



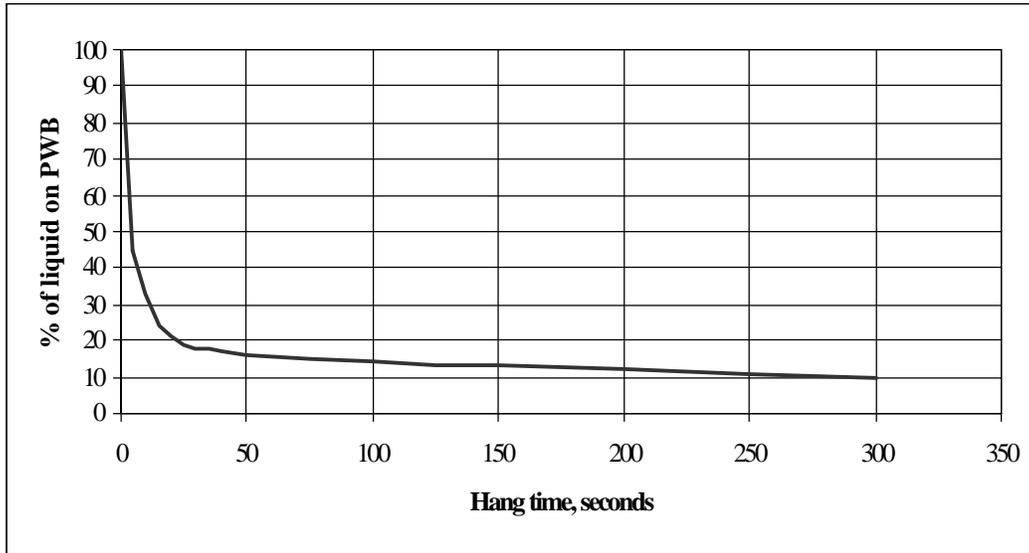
**Figure 1. Measured Versus Predicted Drag-Out for Results by Süß (1992).**

Süß commented that the equations do not account for electrolyte that adheres to the surface and bottom edge even after long drain times, i.e., there is a minimal film thickness left. This becomes increasingly important for rougher surfaces. Süß recommended that drag-out estimations for use in recycling procedures and wastewater treatment should be based on measurements rather than calculations. Part of the reason that poor correlation was found between Süß's measured drag-out and the predictive equations is that Süß's drag-out showed little variation with viscosity as shown in Figure 2.



**Figure 2. Measured Drag-out as a Function of Kinematic Viscosity for Results of Süß (1992).**

McKesson and Wegener (1998) at RD Chemical Company experimentally measured the amount of drainage from PWBs as a function of time. They pointed out that longer “hang” or drainage times allows more liquid to drain from the PWB with consequently less drag-in into the rinse tanks and thus more efficient rinsing. However, too long of a drainage time may result in lower PWB quality due to drying and tarnishing. McKesson and Wegener tested two outer layer boards with solder mask and solder plated and one inner layer board with no holes. A typical result is shown in Figure 3. (This figure is reconstructed from a figure in McKesson and Wegener.)



**Figure 3. Drainage vs Hang Time (McKesson and Wegener 1998).**

The results for all three PWBs lay virtually on top of each other in Figure 3. The authors chose to report just the percentage of liquid that remains on the board rather than mass or volume. This allowed the authors to see the great similarities in drainage among varying conditions. The figure shows two drainage phases. For short times, the liquid drains very quickly followed at longer times by a much slower drainage rate. The authors concluded that 30 seconds appeared to be an optimal drain time. The authors also studied the effect of surfactants and found very little difference. They also tested canting the boards at about a 15-20° angle and saw only minor differences.

It appears that the most influential reference for typical drag-out volumes is the *Electroplating Engineering Handbook* (Pinkerton 1984). These values seem to go back to work by Soderberg published in 1936. Typical drag-out volumes are given in Table 6 as reported by Pinkerton.

**Table 6. Drag-Out per Unit Area (Pinkerton 1984).**

Condition	Drag-Out mL/m <sup>2</sup>
Vertical parts, well drained	16.2 <sup>1</sup>
Vertical parts, poorly drained	82
Vertical parts, very poorly drained	160
Horizontal parts, well drained	32
Horizontal parts, very poorly drained	410
Cup shaped parts, very poorly drained	320-980

<sup>1</sup> Suggested by Pinkerton as being the absolute minimum for drag-out on a vertical sheet.

Hanson and Zabban (1959) discussed the design of a wastewater treatment plant at an IBM plant. To design the plant, an estimate of the wastewater quality was needed. Because a primary source of the contaminants was the plating lines, the drag-out was estimated based on information published by Graham in the *Electroplating Engineering Handbook*. (Note: the data given are the same as that in a more recent version of the *Handbook* given by Pinkerton [1984] and experimental data from another IBM plant which showed drag-out volumes ranging from 100 to 160 mL/m<sup>2</sup>.) For design, a drag-out value of 200 mL/m<sup>2</sup> was used.

Yost (1991) studied the effect of various rinsing arrangements on the costs of cadmium electroplating wastewater costs. In doing the calculations, Yost arbitrarily assumed drag-out of 200 mL/m<sup>2</sup> with no reference for the value.

Chang and McCoy (1990) used a drag-out value of 160 mL/ft<sup>2</sup> to evaluate waste minimization for PWB manufacture. No source was given for their drag-out value, but this value appears to be commonly used by several researchers.

### **Discussions with Experts in the Surface Finishing Industry**

Contacts were made with several experts in the surface finishing industry. One expert source (Sharp 1998) had the following comments on drag-out:

- CH<sub>2</sub>M-Hill did a drag-out study for Merix Corporation sometime in the mid-80s (our efforts to obtain the report from Merix were unsuccessful). CH<sub>2</sub>M-Hill used a bath tank and one rinse tank and dipped the boards in the bath and rinsed them sequentially and monitored the conductivity of the rinse tank. The boards were vertical and had **no** holes (interlayer boards about 20 mils thick), but the hang time and other variables can only be found in the original report. The amount of drag-out was 7½ gallons of process bath liquid per 3,000 ft<sup>2</sup> (102 mL/m<sup>2</sup>) of board area (one side only).
- Holes make a difference for drag-out since the holes are small enough that the liquid does not drain out of them very well. “Hang time” also affects the drag-out.

- Horizontal lines have drag-out of about 2-5 gallons per 3,000 ft<sup>2</sup> (39-66 mL/m<sup>2</sup>) of board area (one side only) for boards with no holes. The drag-out is lower for horizontal lines compared to vertical lines because of the rollers used to squeegee the water off. Vertical boards are the older process, and the trend is to go to horizontal boards. Currently, the industry is about ½ vertical and ½ horizontal.
- One vendor has suggested that the drag-out is about 15 gallons per 3,000 ft<sup>2</sup> (200 mL/m<sup>2</sup>) of board area (one side only). However, this appears too high because the expert's mass balances on his own plating line didn't work out using this number.
- Based on the mass balances on the expert's surface finishing line, i.e., accounting for the amount of chemicals added, consumed, and those in the waste, etc., the drag-out ought to be about 7 gallons per 3,000 ft<sup>2</sup> (95 mL/m<sup>2</sup>) of board area (one side only) for circuit boards with holes, and about 3 gallons per 3,000 ft<sup>2</sup> (41 mL/ft<sup>2</sup>) for interlayer boards.
- There are not any available computer models that could be used to predict wastewater concentrations, flows, etc. for plating lines.

Most of the baths used at the expert's facility (Sharp 1998) have a specific gravity of about 1.08, but the the viscosity and surface tension are unknown. The expert thought that chemical supply companies know the viscosity or surface tension of the process baths, but it is nearly impossible to get those data from the suppliers.

### **Summary of Drag-Out Studies**

Table 7 summarizes the reported drag-out quantities from researchers and practitioners.

**Table 7. Summary of Reported Drag-Out Volumes in the Literature.**

Board Orientation	Bath	Conditions/Description	Drag-Out, mL/m <sup>2</sup>	Reference
Vertical	Microetch	Baseline	130	Pagel 1992
"	"	Slow withdrawal rate	72	"
"	"	Intermediate withdrawal rate & longer drain time	76	"
"	Electroless	Baseline	65	"
"	"	Slow withdrawal rate	32	"
"	"	Intermediate withdrawal rate & longer drain time	31	"
Vertical	Not specified	CH <sub>2</sub> M-Hill study	103	Sharp 1998
Horizontal	"	Based on experience	27 - 67	"
Vertical	"	Boards with holes	95	"
"	"	Interlayer boards without holes	41	"
"	"	Vertical parts, well drained	16 <sup>1</sup>	Pinkerton 1984
"	"	Vertical parts, poorly drained	82	"
"	"	Vertical parts, very poorly drained	160	"
"	"	Rack plating (used to estimate metals in wastewater for design of wastewater treatment system)	203	Hansan & Zabban 1959
Not specified	Not specified	Drag-out value assumed in order to compare costs of rinsing alternatives	162	Yost
"	"	Drag-out value assumed to evaluate waste minimization	160	Chang & McCoy 1990
Vertical	19-20 g/L & 240-250 g/L CrO <sub>3</sub>	Studies at varying drainage angles, drainage times, and withdrawal rates	12 - 65	Süß 1990
Vertical	Various electrolytes	Experimental determinations to test theoretical equations	18 - 94	Süß 1992

<sup>1</sup> Suggested by Pinkerton as being the absolute minimum for drag-out on a vertical sheet.

### Drag-Out Prediction Equations

Kushner (1951a) was one of the first researchers to study drag-out in detail. Kushner distinguished two stages in the generation of drag-out. The first stage is the “withdrawal” stage in which the work piece is moving out of the liquid but is still in contact with it. The second stage is “drainage” in which the work piece is completely out of the liquid, but is still over the bath and liquid is still running off the piece. Kushner considered the withdrawal stage the more important, because the withdrawal determined the thickness of the adhering liquid film. The factors that

control the film thickness are the velocity of withdrawal, viscosity of the liquid, density of the liquid, and surface tension of the liquid although he believed surface tension was a minor factor. Using dimensional analysis, Kushner derived the following equation:

$$f = K \left( \frac{Vm}{\rho g} \right)^m \quad \text{Eqn 5}$$

where:

f	=	film thickness
K	=	unknown constant determined by experiments
V	=	velocity of withdrawal
$\mu$	=	viscosity
$\rho$	=	density
g	=	acceleration of gravity
m	=	unknown exponent determined by experiments

Based on experimental work of others, Kushner concluded that the best fit equation was equation 3 presented earlier:

$$f = 0.02 \sqrt{n \cdot v_A} \quad \text{Eqn 3}$$

Note that although equation 3 was derived by dimensional analysis, it does not appear dimensionally consistent, because the acceleration of gravity is dropped as a term. This is also the equation referenced by Pinkerton and Graham in the *Electroplating Engineering Handbook* (1984). Importantly, this equation is for work pieces with smooth surfaces, unlike PWBs which have many small holes. This equation will tend to underestimate drag-out for PWBs. Notably, this is one of two equations tested by Süß (1992) and discussed above. The equation performed poorly in predicting drag-out for a variety of electrolytes.

Kushner (1951b) argued that equation 3 gives good drag-out predictions for short drainage times, but increasingly overestimates the drag-out with longer drainage times, because it does not allow for the liquid that drains off the work piece. Conceptually for a rectangular sheet, the volume of liquid that drains off the sheet is:

$$\Delta V = A \cdot f_{dr} = A \cdot F_{dr}(f, r, g, m, S, t_{dr}) \quad \text{Eqn 6}$$

where:

V	=	volume of liquid that drains from the rectangular sheet
A	=	area of the sheet
$f_{dr}$	=	thickness of the film that drains off the sheet
$F_{dr}$	=	function describing a relationship between the independent variables and thickness of the film that drains from the sheet
$r_{dr}$	=	surface tension of the liquid
$t_{dr}$	=	drainage time

Hence, the net film thickness or the drag-out volume per unit area after any drainage time,  $t_{dr}$ , is:

$$f = 0.02\sqrt{n \cdot v_A} - F_{dr}(f, r, g, m, s, t_{dr}) \quad \text{Eqn 7}$$

The volume of liquid that drains from the board is a complex process and Kushner was not able to develop a predictive equation. He did, however, make qualitative statements about the effect of several variables. Kushner believed that viscosity was the most important property of the plating solution. Higher viscosities tend to increase the liquid adhering to the sheet as it is withdrawn from the bath and tend to decrease the liquid that drains. Some chemicals in particular are surface active and have molecular structures that increase viscosity. These chemicals may cause a “surface viscosity” that give higher drag-out. Higher densities tend to decrease the liquid adhering to the sheet and increase the drainage. However, the increase in density due to a higher concentration of chemicals in solution is usually outweighed by the increase in viscosity. Kushner gave an example of increasing a sucrose solution from 20% to 60%. This increases the density by 18% while the viscosity increases by 2700%. Lower surface tension will thin the film thickness as the sheet is withdrawn and also increase the drainage as well as reducing the volume of the bead of liquid along the bottom edge of the sheet. Of course, wetting agents are surface active and will concentrate in the drag-out, and hence will be removed at a higher rate than other chemicals. Longer withdrawal times and drain times will reduce drag-out, but Kushner believed that it is better to have a longer withdrawal time than a longer drain time. His rationale was to start with the smallest volume on the work piece to begin with. He also referenced work by Soderberg that drainage times beyond 60 seconds have little effect. Finally, Kushner recommended that work pieces be oriented to minimize the drainage distance and that the pieces be tilted.

### Rinsing Theory

The primary source of the quantity of wastewater generated is rinse water. Most process baths are followed by two rinses, but sometimes just one rinse and sometimes three rinses. The development of rinsing theory can be traced at least as far back as Kushner (1949). Pinkerton and Graham (1984) summarized some of the fundamental mathematical relationships for rinsing. For a non-running rinse tank and assuming that ideal, instantaneous mixing occurs, the concentration of a contaminant in the rinse tank is given by:

$$C_t = C_o \cdot \left[ 1 - \left( \frac{V_t}{V_t + D} \right)^n \right] \quad \text{Eqn 8}$$

where:

- $C_t$  = concentration of contaminant in rinse tank after t min
- $C_o$  = concentration of contaminant solution being drug into rinse tank
- $V_t$  = volume of rinse tank
- $D$  = volume of drag-over or drag-out on rack and work rinsing operation
- $n$  = number of rinsing operations in t min

Most rinse operations at larger facilities use multiple countercurrent cascade rinses. In this case, the concentration in the effluent from the  $r^{\text{th}}$  rinse tank is:

$$C_r = \left[ \frac{(Q \cdot t / D) - 1}{(Q \cdot t / D)^{r+1} - 1} \right] \cdot C_0 \quad \text{Eqn 9}$$

where:

- $C_r$  = concentration of contaminant in the effluent of the  $r^{\text{th}}$  rinse tank
- $Q$  = rate of fresh water flow
- $t$  = time interval between rinsing operations
- $r$  = number of rinse tanks in series

Talmadge (1968) presents equations similar to the above but with an extra term to account for imperfect mixing, i.e., imperfect removal of the contaminant from the work piece.

An approximate equation for multiple, countercurrent rinses has apparently been used by some (Hanson and Zabban 1959; Mohler 1984):

$$Q = \frac{D}{t} \left( \frac{C_o}{C_r} \right)^{1/r} \quad \text{Eqn 10}$$

Mohler (1984) discussed how rinsing equations can be used in practice. In general the rinse must not cause a loss in product quality. There is, then, a maximum allowable concentration in the final rinse called the “contamination limit.” The ratio of the concentration in the drag-in,  $C_o$ , into the first rinse tank (or drag-out from the process bath) to the concentration in the final rinse,  $C_r$ , is the dilution factor or “rinsing ratio,”  $C_o/C_r$ . Either the contamination limit or rinsing ratio can be used to calculate the required rinse flow rate if the other parameters are known. For example, assume that the rinsing ratio is 5,000, there are two countercurrent rinse tanks, the drag-out volume is 100 mL/m<sup>2</sup> of PWB, each rinse cycle rinses 15 m<sup>2</sup> of PWBs, and the time interval between operations is 3 minutes. Then:

- $C_o/C_r$  = 5000
- $D$  = (100 mL/m<sup>2</sup>)(15 m<sup>2</sup>) = 1.5 L
- $t$  = 3 minutes
- $r$  = 2 tanks

Solution of equation 10 yields the required rinse flow rate,  $Q = 35.4$  lpm.

The approach above is consistent with Kushner (1949). Kushner observed that the purpose of the rinse tanks are to “stand guard between baths to keep one solution from mixing with another and contaminating it.” The rinse water flow rate partially determines the concentration of carryover into the next plating tank and thus the plating quality. Kushner believed that each rinse system in a facility would have its own unique rinsing ratio,  $C_o/C_r$ . Kushner suggested several values for the rinsing ratio as listed in Table 8. These values would not be valid to use for PWB manufacturing because it is a different system than what Kushner dealt with and Kushner gave these criteria as approximations based on only limited data, but probably on the conservative side.

**Table 8. Kushner’s (1949) Suggested Rinsing Ratios.**

Type of Rinse Tank	Rinsing Ratio
Rinse after alkaline cleaner	5000 - 7000
Rinse after acid dip	2000 - 3000
Rinse after cyanide dip	3000 - 5000
Rinse after cyanide copper	1500 - 2500
Rinse before drying (better work)	10,000
Rinse before drying (cheaper work)	5,000

Kushner (1979) observed that the theoretical rinsing equations as discussed above assume ideal mixing. Kushner cited work by Talmadge showing that if mixing is very poor so that mixing is by diffusion only, then the equations based on ideal mixing can not be used. However, Kushner stated that experience had shown for most practical applications that the ideal mixing equations were more accurate than equations based on diffusion as the dominant mixing mechanism. Indeed, Talmadge and Buffham (1961) stated that if the primary concern is to estimate the amount of contaminants that enter the wastewater, then rinsing equations based on complete mixing would be adequate and provide conservative answers.

Although using rinsing ratios and the rinsing equations is an interesting approach to calculating the volume of rinse water, it is apparently difficult to do this in practice. The contamination limits are apparently not readily known and are influenced by upstream processes. This was also pointed out by McKesson and Wegener (1998) who stated that there is not standard for rinsing that can be used to determine “manageable” concentrations of contaminants remaining on the work. What is manageable would need to be determined for each specific process and would depend on:

- “The type of contaminant.”
- “The tolerance of the following process step for the particular contaminant in question.”
- “The effect the residual contaminants have on the work.”

## Other Rinsing Theory Studies

Several other rinsing theory studies have been conducted by various researchers. Some of these have focused on how well the drag-out is dispersed into the rinsing tank. While interesting, these studies are not applicable to this project, because sufficient rinsing is used in practice such that most of the drag-out ends up in the rinse water and thence the wastewater. For example, Talmadge and Sik (1969) developed equations to describe the dispersing of the bead of liquid at the bottom of a plate into the rinse water. They extended previous work that used diffusion theory to predict the residual contaminant on a plate in a rinse tank. Talmadge and Buffham (1961) and Talmadge et al. (1962) made detailed investigations of rinsing effectiveness in the absence of mixing or agitation other than the flow of rinse water in the tank, i.e., molecular diffusion is the dominant mass transfer mechanism. They found in such cases that about 10% of the contaminant is left in the film a flat sheet as compared to typically less than 0.1% when using ideal mixing rinse equations. However, the situation is not typical of practice, and as mentioned above, using the ideal complete mixing equations gives a conservative estimate of contaminant in the wastewater, i.e., less contaminant is left on the board.

## PWB Pollution Prevention and Control Technology: Analysis of Updated Survey Results

As part of an EPA funded project, a questionnaire survey form on pollution prevention was sent to 400 PWB shops in 1995 and 40 shops responded. A shortened survey was sent in 1997 to 250 PWB shops in California and 45 responded for a total of 85 between the two surveys. A summary of information relevant to this project follows (U.S. EPA 1998).

Wastewater generation. Most of the wastewater generated is from rinsing. The best estimate of water usage is 10 gallons/(layer-ft<sup>2</sup> of production) or 410 l/m<sup>2</sup> which is the “wetted” surface area and was “calculated based on the total surface area of all layers of boards manufactured.” This value is the mean of the 20 largest shops. Large shops had the most reliable data. Smaller shops were encouraged to estimate their data if they did not know, and this made their data suspect.

Recycle, recovery, and bath maintenance. The survey revealed several practices for recycle, recovery, and bath maintenance:

- Nearly all shops responding to the survey reported using off-site recycling for one or more of their spent process baths although the percentage recycled for each bath type was not reported. The most common bath sent for recycle was spent etching because the baths have high copper concentrations of about 150 g/L. About 80-85% of the responders used an ammoniacal etchant and most of the rest used cupric chloride. The volume of spent ammoniacal etchant solutions generated was 1 gallon per 30 ft<sup>2</sup> (1.4 l/m<sup>2</sup>) of inner- and outer-layer panels. Other types of spent baths were far less likely to be sent off-site for recycle. Tin and/or tin-lead stripping solutions were the next most common spent bath sent off-site and was reported by 20% of the survey responders. Approximately 50% of the responders used a tin outer-layer etch resist and 50% used a tin-lead etch resist. Only 10% of responders indicated that spent rack stripping solutions are sent off-site.

This stripping solution results from removing plating deposits from racks used to hold the PWBs. This solution can be a significant waste. Based on the survey report, we will assume that only spent etchant baths are sent off-site for recycle.

- The use of various technologies to recycle and recover baths and waste streams on-site varied. Ion exchange was used by 45% of the responders to treat and recover discharges, but many times this was part of their waste treatment system.
- The volume of wastes generated from spent baths was estimated as shown in Table 9.

Wastewater treatment. Wastewater treatment systems removed the metals by conventional precipitation systems, ion exchange, or a combination of the two. Wastewater treatment sludges generated are typically (88% of responders) sent off-site for recycle rather than disposed of in a landfill. Sludge generation data were few. The three largest facilities reporting data had sludge generation rates of 0.02, 0.31, and 0.24 kg/m<sup>2</sup>. The smallest number, 0.02 kg/m<sup>2</sup>, came from a facility making only single sided boards whereas the other two had a larger mix of products which generated more waste.

Drag-out reduction practices. Table 10 shows the drag-out reduction or recovery practices used by the responders.

Drag-out reduction can reduce pollution, but it can cause problems for the process baths due to greater build-up of contaminants in the bath. One or more bath maintenance techniques may be required.

### **Water Use Rates from Survey of MHC Facilities**

As part of a U.S. EPA sponsored research project, the University of Tennessee CCPCT (1997) surveyed MHC PWB plating facilities. Part of the survey addressed water use for various MHC process alternatives. Table 11 shows the estimated water consumption for MHC alternatives based on the survey data and normalizing assumptions.

These water consumption rates are of the same order of magnitude as those from the U.S. EPA (1998) survey discussed earlier which estimated water usage to be 10 gallons/(layer-ft<sup>2</sup> of production) as the mean of the 20 largest shops.

**Table 9. Selected Waste Volume Estimates From Spent Baths.**

Process	Waste	Volume <sup>1</sup> (per 1,000 ft <sup>2</sup> of 4 layer boards)	Volume <sup>1</sup> (per m <sup>2</sup> of 4 layer boards)
Etching, inner and outer layers	Spent etchant	140 gallons	5.7 liters
Dry film resist developer	Spent developer	200 gallons	8.1 liters
Dry film resist stripper	Spent stripping solution	6 gallons	0.24 liters
Tin-lead stripper	Spent stripping solution	17 gallons	0.69 liters
Soldermask developer	Spend developer	60 gallons	2.4 liters
Microetch; inner and outer layers	Spent micro-etchant	16 gallons	0.65 liters
Sulfuric acid dips	Spent sulfuric acid baths	12 gallons	0.48 liters
Electroless copper	Waste electroless Cu bath	26 gallons	1.1 liters
Board trim	Waste copper-clad material	187.5 ft <sup>2</sup> , 42.9 lbs Cu	0.1875 m <sup>2</sup> , 19.6 kg

<sup>1</sup> Assumptions:

- a) Ammoniacal etchant used for both inner- and outer-layers, 70% of copper foils etched, 1 oz. copper used on all layers, and 20 oz/gal carrying capacity of etchant.
- b) 50% of film developed (30% outer, 70% inner), developer carrying of 3 mil-ft<sup>2</sup>/gal, and 1 mil film is used throughout.
- c) 50% of film stripped (70% outer, 30% inner), stripper carrying capacity of 100 mil-ft<sup>2</sup>/gal, and 1 mil film is used throughout.
- d) 30% metal area, tin-lead resist is 0.3 mil thick and stripper capacity of 15 oz/gal of metal.
- e) 30% of mask developed, 1 mil thickness, 10 mil-ft<sup>2</sup>/gal carrying capacity.
- f) Oxide, electroless Cu, and pre-pattern plate microetches (50%, 100%, and 30% of surface area etched, respectively) considered. Many facilities may employ additional baths.
- g) Microetches average etch and 4 oz/gal carrying capacity.
- h) Bath life of 1 gallon/500 ssf, 3 sulfuric dips (oxide, electroless copper, and pattern plate lines).
- I) 18x24 panels with 0.75 inch thief area and 0.25 inch spacing of 6 step-and-repeats, outer layer 2 oz copper (80% trim area), inner layer 1 oz copper (50% trim area).

**Table 10. Drag-out Reduction or Recovery Practices Used by the Responders.**

Drag-Out Reduction or Recovery Practice	PWB Responders Using, % <sup>1</sup>	Plating Shops Using, % <sup>2</sup>
Allow for long drip times over process tanks	76.3	60.4 <sup>3</sup>
Have drip shields between process and rinse tanks	60.5	56.9
Practice slow rack withdrawal from process tanks	52.6	38.1 <sup>3</sup>
Use drag-in/drag-out rinse tank arrangements	34.2	20.8 <sup>3</sup>
Use drag-out tanks and return contents to process baths	34.2	61.0 <sup>3</sup>
Use wetting agents to lower viscosity	31.6	32.4
Use air knives to remove drag-out	26.3	2.2 <sup>3</sup>
Use drip tanks and return contents to process baths	10.5	27.0 <sup>3</sup>
Use fog or spray rinses over heated process baths	10.5	18.9 <sup>3</sup>
Operate at lowest permissible chemical concentrations	7.9	34.6
Operate at highest permissible temperatures	5.2	17.9

<sup>1</sup> Data from PWB survey.

<sup>2</sup> Data from 1993-1994 survey of for the metal finishing industry.

<sup>3</sup> Data are for manually operated methods, which are the predominant type for the plating operations surveyed during the NCMS/NAMF project.

**Table 11. Water Consumption Rates of PWB MHC Alternatives.**

Process Type	Water Consumption <sup>1</sup>	
	(gal/ft <sup>2</sup> )	(l/m <sup>2</sup> )
Electroless copper, non-conveyorized	11.7	476
Electroless copper, conveyorized	1.15	46.8
Carbon, conveyorized	1.29	52.5
Conductive polymer, conveyorized	0.73	30
Graphite, conveyorized	0.45	18
Non-formaldehyde electroless copper, non-conveyorized	3.74	152
Organic-palladium, non-conveyorized	1.35	54.9
Organic-palladium, conveyorized	1.13	46.0
Tin-palladium, non-conveyorized	1.80	73.2
Tin-palladium, conveyorized	0.57	23

<sup>1</sup> Based on wetted board surface area.

## RESEARCH APPROACH

The objective of this study was to develop and validate methods to predict the quality of waste water generated from PWB manufacturing processes. The methods can then be used to compare alternative manufacturing processes in the PWB industry. In the DFE studies, industrial and environmental exposure and risk are evaluated on a chemical-specific basis for individual manufacturing operations. Wastewater data collected during routine regulatory sampling are inadequate for these purposes because data are collected for only a few specific pollutants and the samples contain wastewater from the entire plant rather than an individual process line. For these reasons, a mass-balance calculation is the most suitable approach to estimating the load of each pollutant emanating from a given process line.

The literature review revealed that drag-out was the source of most of the contaminants in the wastewater from a given process. Process-specific waste loads originating from drag-out can be estimated by the product of the drag-out volume and the chemical concentration in the process baths. The latter are determined as an existing component of the DFE process. However, according to the literature review, drag-out volume from PWBs and other flat, vertical pieces can vary between about 10 and 120 mL/m<sup>2</sup>. Drag-out was affected by variables such as bath chemistry, board withdraw rate, drain time, and orientation of the boards during withdraw. Board surface characteristics and the number and geometry of holes drilled in the board may also be significant, but these variables have not been systematically investigated to date. Equations presently available in the literature fail to accurately predict the volume of drag-out from vertical plates (Süß 1992).

The MHC process was selected as the basis of the research because a significant data base already existed for this process as a result of the previously concluded DFE project. Also, the research team was most experienced and familiar with this process line. The results of this work apply to other PWB processes that employ process baths in which the boards are vertically oriented.

The specific steps in the research plan were:

- To conduct limited laboratory drag-out experiments for the purpose of supplementing existing data in the literature.
- To identify or develop an accurate and comprehensive drag-out model for PWB using a data-base that includes data developed in this study and by others.
- To develop a computer model to predict wastewater quality and quantity from a PWB processes that incorporates the new drag-out model.
- To validate the model using data from process bath and rinse water samples collected from three MHC process lines.

## LABORATORY DRAG-OUT EXPERIMENTS

Laboratory drag-out experiments were conducted to supplement existing drag-out data in the literature. Existing drag-out equations do not accurately predict the effect of fluid properties on drag-out from vertical flat pieces such as PWBs (Süß 1992). While some studies have investigated the effect of viscosity, another parameter that may exert significant influence, surface tension, has received virtually no attention. The scope of this study did not allow a comprehensive evaluation of the effect of these parameters. Instead, an alkaline cleaner bath was selected as a bath that was more difficult to drain and a microetch bath was selected as one that would be relatively easy to drain. During the study, viscosity and surface tension would be measured to gain an indication of the relative influence of these parameters on drag-out.

The procedures for the laboratory drag-out experiments were devised to simulate conditions occurring in the PWB manufacturing process. The drag-out volume was measured gravimetrically as the boards were withdrawn from the process tanks. Experiments were conducted using two heated process baths to determine the range of expected drag-out volumes under various conditions. Because the alkaline cleaner/condition and microetch baths have significantly different chemical compositions and properties, these baths were chosen for the experiments to provide a realistic range of drag-out volumes. The board size was 0.457 m by 0.610 m. Experimental conditions that were studied were the orientation of the board during the drain time, the length of the drain time, the board withdraw rate from the bath, and shaking the board at the beginning of the drain period. Withdraw rates of 0.076 m/sec and 0.305 m/sec were tested, and the boards were drained with the long edge horizontally, vertically, or at a 45° angle. Drain periods of 10 seconds, 20 seconds, and 30 seconds were studied. The basic operating conditions (BOC) for the majority of the tests were: 0.076 m/sec withdraw rate, 10 second drain time, no shaking after board withdraw, 45° drain angle, and the board oriented with the long edge horizontal. Nine sets of experiments were conducted on each bath for a total of eighteen drag-out experiments. Several additional experiments were conducted with the microetch bath for a drilled board with a different hole density and design. The matrix of experimental conditions that were tested for each of the two baths is presented in Table 12.

For the alkaline cleaner/conditioner experiments, generally five repetitions were made for each condition, with the circuit board remaining submersed in the bath for one minute on each test. Since the etching process changed both the properties of the circuit board and the chemical composition of the bath, only three repetitions for each condition were performed and the boards were only allowed to remain submersed for 30 seconds. These conditions were taken into account by assuming that the copper etch rate would remain constant over the duration of the experiments. This assumption was verified by weighing the boards before and after the tests to determine the mass of copper etched from the board.

**Table 12. Experimental Matrix for Laboratory Study of Drag-out Volumes for Each Bath Type.**

<b>Experimental Conditions</b>	<b>Drilled Board</b>	<b>Undrilled Board</b>	<b>Drilled, Etched Board</b>
0.076 m/sec withdraw 45° drain angle 10 sec drip time no shaking	!	!	!
0.076 m/sec withdraw long edge horizontal 10 sec drip time no shaking	!		
0.076 m/sec withdraw long edge vertical 10 sec drip time no shaking	!		
0.076 m/sec withdraw 45° drain angle 20 sec drip time no shaking	!		
0.305 m/sec withdraw 45° drain angle 30 sec drip time no shaking	!		
1.0 fps withdraw 45° drain angle 10 sec drip time no shaking	!		
0.076 m/sec withdraw 45° drain angle 10 sec drip time shake board	!		

*Apparatus*

- 10 cm by 61 cm by 76 cm high density polyethylene (HDPE) tank, supported and stabilized to prevent tipping.
- Magna-Whirl Constant Temperature Water Bath, Model MW-1140A-1.
- Pump, ITT Jabsco Self-Priming, Model 12290-0001, 115 volt, 3.3 amp, with thermal overload protection.
- 6 m of 1.3 cm diameter stainless steel tubing, coiled to fit inside bottom of HDPE tank.
- 1.3 cm I.D. Nalgene tubing, lab/food grade, with connection clamps.
- 48 liters bath solution (Alkaline Cleaner/Conditioner or Microetch).
- Mettler Toledo Electronic Analytical Balance, Model PR5002, Maximum 5100 grams, with cardboard air current shield.

- 0.457 m by 0.610 m circuit boards (copper clad with holes; copper clad without holes; etched, with holes).
- Plastic bags, 0.50 mil, 110 l capacity.
- Whittner Taktell Super-Mini Metronom, Model 886051, set at 120 beats per minute.
- Laboratory clamps and clips.

### *Procedure*

1. For the first set of experiments, the Alkaline Cleaner/Conditioner bath was prepared according to the manufacturer's specifications by filling the HDPE tank with 24 L of deionized water. Next, 2.88 L of Electro-Brite ML-371 were added, and the tank was brought to a volume of 48 L with deionized water to produce a 6% (by volume) concentration. The solution was gently mixed. For the second set of experiments, the Microetch bath was prepared according to the manufacturer's specifications by filling the HDPE process tank with 24 L of tap water and adding 720 g of copper sulfate pentahydrate ( $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ ) and 8.64 L of 66° Baume sulfuric acid ( $\text{H}_2\text{SO}_4$ ). The acid was added very slowly, taking care that the temperature of the mixture remained below 54° C. A laboratory thermometer was inserted into the mixture to monitor temperature. Next, 3.34 L of Co-Bra Etch Inhibitor Makeup were added, and the mixture was brought to a volume of 48 L with tap water.
2. The stainless steel heating coil was placed into the HDPE tank containing the simulated bath. The coil inlet was connected to tubing from the water bath (with the in-line pump), and the coil outlet connected to tubing discharging back to the water bath. The experimental set up is presented as Figure 4.
3. The Magna-Whirl water bath was filled with approximately 95 liters of hot tap water. The water bath heater and pump were turned on, allowing the bath to equilibrate to 57° C for the alkaline cleaner/conditioner, and 52° C for the microetch bath. The water bath thermostat was set, and a thermometer was placed in the bath to monitor the bath temperature.
4. The bath temperature, pH, and density were measured *in-situ* in the tank. Conductivity, viscosity, and surface tension were measured on a sample collected from the tank. Analyses were performed as described later in the section entitled: **COLLECTION AND ANALYSIS OF FIELD SAMPLES.**
5. The circuit board was cleaned with tap water and detergent, and thoroughly rinsed with deionized water. The board was dried using compressed air to ensure no moisture remained entrapped in the holes.
6. The board was centered on the analytical balance, and the weight was recorded to the nearest 0.01 g.
7. A clean new plastic bag was weighed on the analytical balance, and the results recorded to the nearest 0.01 g.
8. The plastic bag was opened, and carefully attached to the outside of the HDPE tank using small laboratory clips.

9. The metronome was turned on, and two laboratory clamps were attached to the circuit board to serve as handles. The circuit board was slowly lowered into the tank so the entire surface was completely submerged in the bath. The board was agitated slightly to remove entrapped air bubbles, and then allowed to remain submerged for approximately one minute in the alkaline cleaner/conditioner bath or 30 seconds in the microetch bath. The process was timed by counting ticks on the metronome.
10. The board was removed vertically at the appropriate withdraw rate, stopping several inches above the bath surface. Depending on the experiment, the board was then either held steady or given one quick shake, and the board held so that its edge was either level or at a 45° angle during the allotted drain time. The appropriate withdraw rates, drain positions, and drain times were specified in the Table 12. Both the withdraw rate and drip time were timed by ticks of the metronome.
11. The board was immediately placed into the plastic bag attached to the tank. Extra care was taken to ensure that any drips after the specified drain period fell into the bag, and that the sharp corners of the board did not puncture the bag.
12. The clamps were removed from the board, along with the clips holding the bag to the tank. The bag was carefully sealed, removing as much air as possible.
13. The sealed bag containing the circuit board and drag-out was centered on the analytical balance and weighed, the results were recorded to the nearest 0.01 g.
14. The circuit board was carefully removed from the bag, and the process was repeated, beginning with weighing a clean new plastic bag.
15. After the specified number of runs were completed for each set of conditions, the bath temperature, pH, and density were again measured *in-situ* in the tank. Conductivity, viscosity, and surface tension were measured on a sample collected from the tank. Analyses were performed immediately after collecting the sample, and the results were recorded.
16. The drag-out volumes were calculated.

Before the actual drag-out experiments were conducted using PWB bath chemicals, a series of four preliminary tests were conducted to validate the proposed methodology and to verify that the drag-out could be measured accurately and precisely. The preliminary tests also served as practice runs, and allowed for any necessary adjustments to the procedure and apparatus. The coefficients of variation for the first two tests were 0.039 and 0.056, for eleven and nine trials, respectively. The coefficients of variation in the third and fourth tests improved to 0.007 and 0.008, respectively, for series of seven trials each. Since preliminary tests were not designed to cover the full range of operating variables, the following representative variables were selected: 1) ambient temperature tap water was used to simulate bath chemicals; 2) a 0.265 m x 0.457 m drilled etched board was used in the first two preliminary tests, and a 0.457 m by 0.610 m drilled copper clad board was used for the third and fourth tests; and (3) the circuit board was withdrawn at 0.15 m/sec, given one quick shake after removal, and allowed to drip for 10 seconds.

## Quality Assurance and Quality Control (QA/QC)

Prior to the experiments, all laboratory equipment was thoroughly cleaned with detergent followed by a thorough deionized water rinse. The analytical balance used for weighing the boards was allowed to warm up for at least 30 minutes before any measurements were made. The balance was calibrated using calibration weights at the beginning and end of each laboratory session, to ensure the instrument had not drifted. A large shield was placed around the balance to decrease the effects of drafts while weighing the board.

Prior to mixing the actual baths, 500 ml batches of the solution were prepared per the manufacturers' product information sheets. Measurements of viscosity, specific gravity, surface tension, conductivity and pH were compared between the 500 ml batches and the full bath volume. Temperature was monitored continuously during the drag-out experiments in the baths by suspending a laboratory thermometer in the tank. Before the tests, the timing of the metronome was checked with a clock to ensure proper timing. The tank was positioned in front of a fume hood for adequate ventilation, and a large strip of tape was affixed to the fume hood shield at a 45° angle from the horizontal to use as a guide during drain periods. Personal protection equipment such as safety goggles, gloves, and aprons were used whenever feasible. All waste material including plastic bags contaminated with the drag-out chemicals and the used bath solutions were stored for proper disposal. All laboratory experimental information and data were recorded in a laboratory notebook, with carbon copies given to the principal investigators upon test completion.

## Results and Discussion

Results of the laboratory drag-out volume experiments are presented in Tables 13 and 14 for the alkaline cleaner/conditioner and microeth baths, respectively.

**Table 13. Drag-Out Results for Alkaline Cleaner/Conditioner Bath.**

Test	Board Type	Drag-Out (ml/sq.m)	Coeff. of Variation
BOC	drilled, design 2	77.8	0.032
BOC, board edge horizontal	drilled, design 2	75.6	0.015
BOC, board edge vertical	drilled, design 2	81.3	0.021
BOC, 20 sec. drip time	drilled, design 2	68.2	0.040
BOC, 30 sec. drip time	drilled, design 2	64.5	0.047
BOC, 1 fps withdraw	drilled, design 2	98.7	0.013
BOC, with shake	drilled, design 2	77.8	0.032
BOC	undrilled	38.6	0.016
BOC	drilled, etched	89.2	0.038

Note: Design 1, 5619 holes; Design 2, 7824 holes.

**Table 14. Drag-Out Results for Microetch Bath.**

Test	Board Type	Drag-Out, ml/sq m	Coeff. of Variation
BOC (2/2/99)	drilled, design 2	108.9	0.043
BOC (2/13/99)	drilled, design 2	107.8	0.023
BOC (2/13/99)	drilled, design 2	93.4	0.038
BOC, board edge horizontal	drilled, design 2	120.9	0.006
BOC, board edge vertical	drilled, design 2	113.0	0.006
BOC, 20 sec. drip time	drilled, design 2	98.1	0.015
BOC, 30 sec. drip time	drilled, design 2	94.4	0.007
BOC, 1 fps withdraw	drilled, design 2	133.1	0.016
BOC, with shake	drilled, design 2	111.9	0.021
BOC	drilled, design 2	69.8	0.038
BOC, etched board	drilled, design 2	112.3	0.022
BOC, etched board	drilled, design 2	118.3	0.021

Note: Design 1, 5619 holes; Design 2, 7824 holes.

The drag-out volume for each experimental condition was calculated using the mean drag-out weight from the group of tests for the specific condition. This was generally five runs for the alkaline cleaner/conditioner, and three runs for the microetch. In addition to calculating the mean drag-out weight (in grams), the standard deviation and the coefficient of variation of the measurements were checked for each condition. The coefficient of variation was less than 0.05 for all experiments.

The mean drag-out volume for all experimental conditions for the alkaline cleaner/conditioner was 74.7 ml/m<sup>2</sup>, which is approximately 30% less than the mean drag-out volume of 108 ml/m<sup>2</sup> for the microetch bath. The mean drag-out for all experimental conditions for both baths combined was 91.1 ml/m<sup>2</sup>, and was calculated using only data from the same board hole design so as not to skew the results. It appears that drain time has an affect on drag-out volume, as reflected in the decreasing drag-out volumes as drain time increased. It also appears that the drag-out volume increases as the board withdraw rate decreases. Board tilt and orientation did not appear to affect the drag-out volume; however, drilled boards had more drag-out than undrilled boards, as expected.

Results from the microetch experiments compare favorably to those performed at Micom, Inc. (Pagel 1992), although a direct comparison was difficult since operating conditions were different. Board hole density for both tests were similar, with Micom boards having 33,000 holes/m<sup>2</sup> compared to 28,000 holes/m<sup>2</sup> for the boards used in the microetch experiments in this study. Pagel's drag-out volumes appear to be less than those measured in this study. At a withdraw rate of 0.20 m/sec and drain time of 12.1 sec, Pagel reported a drag-out volume of 76.4 mL/m<sup>2</sup>. Under similar conditions, specifically a withdraw rate of 0.305 m/sec and a drain time of 10 seconds, this study resulted in a drag-out of 130 mL/m<sup>2</sup>. Other differences in experimental

procedures that could affect drag-out volumes include: 1) a 45° drain angle used in this study, compared to a 0° angle used by Pagel; 2) Pagel’s experiments included drag-out associated with the racks; and 3) drag-out was measured by completely different approaches; specifically, Pagel used a concentration approach whereas this study used a weight approach.

Analyses of parameters for the alkaline cleaner/conditioner and microetch simulated baths were performed before the drag-out tests were run, and again after the tests were completed. Results of the tests are presented in Tables 15 and 16.

**Table 15. Alkaline Cleaner/Conditioner Bath Properties.**

Parameter	Before Experiments	After Experiments
pH	8.65 @ 58°C	8.47 @ 57°C
Conductivity mS/cm	0.21 @ 35°C	0.23 @ 35°C
Specific Gravity	8.65 @ 57°C	0.995 @ 57°C
Surface Tension, dynes/cm	34.7	34.7
Viscosity, cP	0.85	0.87

**Table 16. Microetch Bath Analyses.**

Parameter	Before Experiments	After Experiments
pH	-0.42 @ 53°C	-0.62 @ 55°C
Conductivity mS/cm	1374 @ 22°C	1562 @ 22°C
Specific Gravity	1.175 @ 53°C	1.205 @ 57°C
Surface Tension, dynes/cm	71	60
Viscosity, cP	1.44 @ 49°C	0.87 @ 50°C

As expected, there was no significant variation in the bath parameters for the alkaline cleaner/condition bath comparing values before and after the drag-out tests. There were, however, significant variations in the microetch bath characteristics, as expected. Conductivity, specific gravity, hydrogen ion concentration and viscosity all increased, possibly due to the increase in copper in the bath as a result of etching from the PWBs during the drag-out tests.

## DRAG-OUT MODEL DEVELOPMENT

As stated previously the goal of this project was to develop and validate methods for predicting the quality of wastewater generated during PWB manufacturing. Drag-out and bath dumps are the two major sources of process wastewater. The literature reports drag-out rates for flat panels and PWBs ranging from 10 to 160 ml/m<sup>2</sup>. Currently-available models utilize solution viscosity and withdraw rate as the primary independent variables. Süß (1992) has demonstrated that drag-out rates predicted using these models are poorly correlated with results from experiments. Clearly there is a need for a more accurate means of predicting drag-out for PWB manufacturing.

In addition to the drag-out data collected as part of this study, three data sets containing extensive drag-out data for PWBs or flat panels were available in the literature (Süß 1990; Süß 1992; Pagel 1992; Ducker). An attempt was made to develop regression models to predict drag-out volumes as a function of PWB manufacturing practices. Possible model variables that were either recorded or varied in each study are summarized in Table 17.

**Table 17. Potential Variables for PWB Drag-Out Prediction Model.**

	Süß 1990	Süß 1992	Pagel 1992	This Study
Board Size	.	.	.	.
Withdraw Rate	.	.	.	.
Drain Time	.	.	.	.
Board Orientation	.			.
Board Angle	.			.
Board Surface				.
Holes	.	.	.	.
Shaking or Vibration				.
Bath Type	.	.	.	.
Kinematic Viscosity		.		.
Surface Tension				.

Of the variables listed in the table above, not all were evaluated for inclusion in the model. Board surface (etched or unetched) and shaking were not included in the parameters to be evaluated because the little data that were available for these parameters indicated they have a minor effect on drag-out volumes. Board orientation during draining was also not considered because relatively few data were available and it is not one of the waste minimization practices commonly practiced. We hypothesized that kinematic viscosity and surface tension were two fluid properties that may be most significant in determining drag-out volumes. However, Süß (1992) showed that drag-out volume was poorly correlated with kinematic viscosity. Furthermore, Pagel's data set did not include data for either kinematic viscosity or surface tension of the baths and Süß's data did not include any surface tension data. It was judged that the quantity of data and range of values for these two variables were insufficient to justify their inclusion in the model.

In the data base used to develop the model, board size (m<sup>2</sup>), withdraw rate (m/sec), and drain time (sec) were treated quantitatively by using the numerical value of the variable. Three other variables were treated qualitatively using indicator variables having values of 1 or 0. The indicator variable for board angle was assigned a value of 1 if the board was angled and a value of 0 if the board edge was kept horizontal. Similarly, the indicator variable for holes was assigned a value of 1 if it contained holes and a value of 0 if the board did not contain holes. The hole density for the drilled boards in the data base ranged from 20,000 to 33,000 holes/m<sup>2</sup>; however, data needed to further quantify the effect of drilled holes, such as hole diameter and aspect ratio, were not available. Three different indicator variables were included to specify bath type: alkaline cleaner, micro-etch and electroless copper. The obvious disadvantage of this approach is that the model can make bath-specific predictions only for these three bath types, but insufficient viscosity and surface tension data are available to make the model more general.

The data set was not ideal for development of the model. The work of Süß (1990, 1992) was not specific to the PWB industry; therefore, he did not use standard PWB process baths, his boards were smaller than those often used in the PWB industry, and his boards did not contain drilled holes. As a result, variables describing board size and holes were strongly correlated (0.904), making it difficult to distinguish between the effects of these two parameters. Also, Süß did not use actual PWB process baths, thus bath type and board size were also correlated. During model development, it was necessary to be aware of the effects that these peculiarities may have on the developed model.

Both a linear regression model and a multiplicative regression model were tested. The linear model was:

$$DO = a_0 + a_1 SIZE + a_2 WR + a_3 DT + a_4 \frac{WR}{DT} + a_5 WR \cdot DT + a_6 HOLES + a_7 ANGLE + a_8 ALK + a_9 MICRO + a_{10} ELCTRLS$$

where:

DO	=	drag-out volume, mL/m <sup>2</sup>
SIZE	=	board area, m <sup>2</sup>
WR	=	withdraw rate, m/sec
DT	=	drain time, sec
HOLES	=	1 if the board is drilled and = 0 for undrilled boards
ANGLE	=	1 if the board is tilted during draining and = 0 if the board is kept horizontal
ALK	=	1 if the bath is an alkaline cleaner bath and = 0 otherwise
MICRO	=	1 if the bath is a micro-etch bath and = 0 otherwise
ELCTRLS	=	1 if the bath is an electroless copper bath and = 0 otherwise

The multiplicative model was:

$$DO = a_0 \cdot SIZE^{a_1} \cdot WR^{a_2} \cdot DT^{a_3} \cdot a_6^{HOLES} \cdot a_7^{ANGLE} \cdot a_8^{ALK} \cdot a_9^{MICRO} \cdot a_{10}^{ELCTRLS} \quad \text{Eqn 12}$$

which was rewritten in linear form for analysis by linear regression:

$$\log DO = \log a_0 + a_1 \log SIZE + a_2 \log WR + a_3 \log DT + HOLES \log a_6 + ANGLE \log a_7 + ALK \log a_8 + MICRO \log a_9 + ELCTRLS \log a_{10} \quad \text{Eqn 13}$$

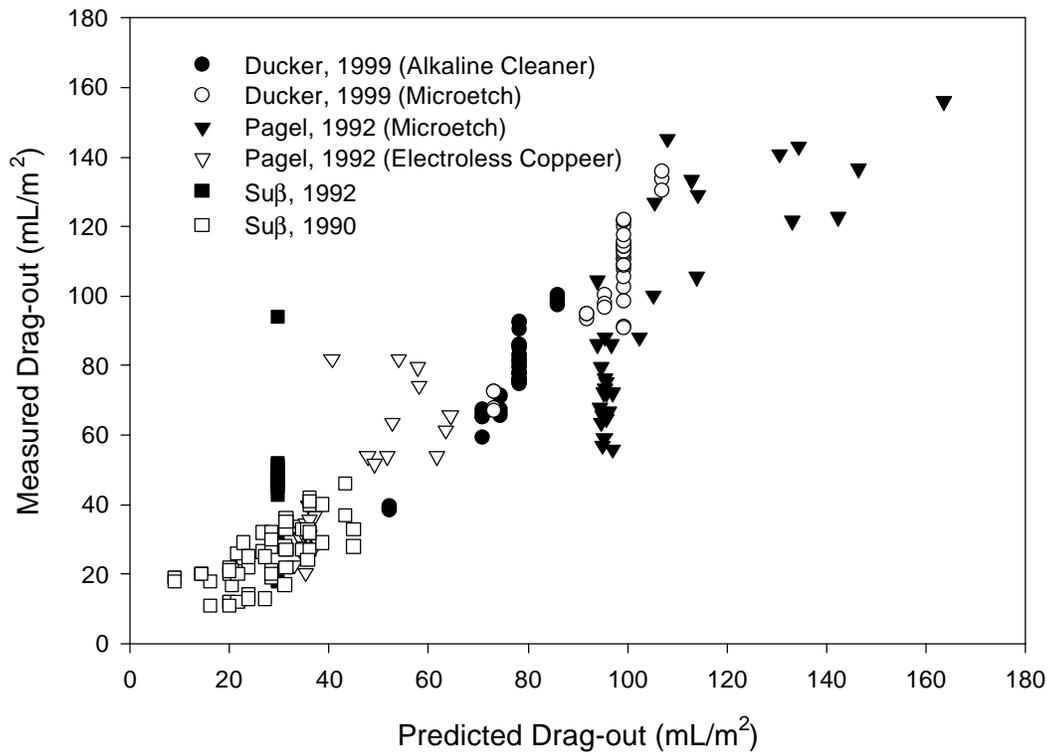
Both models were evaluated using stepwise regression (SPSS ver. 9). This procedure adds or removes independent variables to the model based on criteria related to the reduction in the sum of squares achieved by inclusion of the variable. The final model includes only the variables that result in a statistically significant reduction in the sum of squares error. The stepwise regression procedure yielded an  $r^2 = 0.883$  for the linear model and 0.814 for the multiplicative model. The linear model was:

$$DO = 3.63 + 694 \cdot SIZE - 180 \cdot ELCTRLS + 89.6 \cdot \frac{WR}{DT} - 155 \cdot ALK + 38.6 \cdot HOLES + 29.9 \cdot WR - 0.443 \cdot DT - 127 \cdot MICRO \quad \text{Eqn 14}$$

The statistical package did not include the variables of ANGLE and WR·DT in the model because they were not statistically significant. Inspection of this equation reveals that all three bath-type coefficients are relatively large negative numbers, which would cause it to predict an erroneously large drag-out for large boards (ca. 0.25 m<sup>2</sup>) with bath-types not explicitly accounted for in the model. For small boards (ca. 0.05 m<sup>2</sup>) used with the bath-types accounted for in the model, it could predict negative drag-out values. These anomalies were the result of correlation of the independent variables, as described earlier. To correct this problem it was necessary to eliminate one of the three bath types as a variable in the model. Each of the three bath types was evaluated for elimination, the best fit was given by eliminating MICRO as a variable ( $R^2=0.852$ ). The final drag-out model was:

$$DO = 18 + 201 \cdot SIZE - 60.1 \cdot ELCTRLS + 73 \cdot \frac{WR}{DT} - 20.9 \cdot ALK + 26.0 \cdot HOLES + 26.1 \cdot WR - 0.355 \cdot DT \quad \text{Eqn 15}$$

A comparison of predicted and measured drag-out volumes is shown in Figure 5. The groups of vertically-aligned data points occur when the model predicts a near-constant drag-out for conditions in which the measured drag-out is variable. While some of the variability is random error, some is also the result of variation of the independent variables, indicating that the model is not able to accurately account for all the variables that affect drag-out. A more comprehensive data base in which the independent variables are systematically varied is needed if more accurate predictions of drag-out from PWB manufacturing processes are desired.



**Figure 5. Comparison of Measured and Predicted Drag-Out Volumes.**

## PWB WASTEWATER MODEL

Given the volume of drag-out from and chemical composition of each bath, it is possible to calculate the mass of each contaminant that would enter the waste stream for a given PWB process line. A computer model was developed to facilitate such calculations. The model was based on the following assumptions:

1. Contaminants in wastewater are from drag-out from process baths and from dumping of some baths at the end of their useful life. Contaminants from the stripping of racks from deposits are ignored.
2. Essentially 100% of the drag-out ends up in the wastewater, i.e., very efficient rinsing.
3. Predictions are for vertical boards only.
4. Various predictive equations reported in literature are of limited value for estimating absolute values of drag-out as evidenced by the results of Süß's work comparing predicted versus measured drag-out. Equation 15 was used to estimate drag-out in the model here.
5. Insufficient information exists to include surface tension as a variable although the authors recognize that it may be an important variable.
6. The estimate of drag-out of contaminants in g/d is based on the PWB production rate, chemical composition of each bath, and the estimated drag-out from each bath, according to the following equation:

$$\left( \begin{array}{l} \text{kg / d of} \\ \text{contaminant i} \\ \text{from bath j} \end{array} \right) = \left( \begin{array}{l} \text{PWB production} \\ \text{rate, m}^2 / \text{d} \end{array} \right) \cdot \left( \begin{array}{l} \text{Concentration of} \\ \text{i in bath j, mg / L} \end{array} \right) \cdot \left( \begin{array}{l} \text{drag-out from} \\ \text{bath j, mL / m}^2 \end{array} \right) \quad \text{Eqn 16}$$

The model is coded in an Excel Spreadsheet and utilizes a Visual Basic Macro. The user is required to enter information in a separate spreadsheet defining the operating conditions of the process line and the chemical composition of the baths. The effect of bath dumps on the overall pollutant load can be included by specifying their frequency. The model calculates the mass of contaminants coming from each process tank, together with the contaminant mass and concentration for the entire process line. A user's manual is included in the Appendix.

## COLLECTION AND ANALYSIS OF FIELD SAMPLES

Samples of plating baths and rinse waters were collected from the MHC process line from three different PWB facilities for the purpose of verifying the drag-out model. Three process baths at each plant were selected for sampling: microetch, electroless copper, and Anti-Tarnish. Sodium or potassium were selected as tracers for each bath because they are common ions in PWB baths, and they tend to be relatively stable in solution. The relative amount of sodium and potassium in the bath and downstream rinses can be used to estimate the drag-out from each tank and to verify the overall mass balance approach to modeling wastewater quality from PWB facilities. In addition to sodium and potassium, fluid properties (viscosity, surface tension and specific gravity) that might effect the quantity of drag-out were measured. Routine measurements of conductivity and pH were taken too. The project QA/QC plan (Robinson and Cox 1998), submitted to and approved by EPA, was followed except where field conditions necessitated minor changes.

### Process Characterization

Operating practices affect the amount of drag-out and the concentration of contaminants in the rinse-tank effluent. Extensive data characterizing the operating practices used at each site were collected during the site visits. Operating practices potentially affecting the amount of drag-out or the rinsing process are summarized in Tables 18 - 20. These data were later used to predict the drag-out from each process bath using equation 15 and to independently calculate the drag-out via a dynamic mass balance approach described later.

**Table 18. Summary of MHC Operating Practices for the Field Sites.**

	Cycle Time, min	Withdraw Rate, m/sec	Board Tilt, degrees	Hole Density, #/m <sup>2</sup>
Plant 1	30	0.173	5	100,000 to 570,000
Plant 2	37	0.163	0	NA
Plant 3	27	0.234	0	50,000

**Table 19. Summary of Drip Times for Process Baths at Field Sites.**

Bath	Drip Time, sec
Plant 1 ME	5
Plant 1 EC	25
Plant 1 AT	5
Plant 2 ME	10
Plant 2 EC	15
Plant 2 AT	10
Plant 3 ME	5
Plant 3 EC	10
Plant 3 AT	5

**Table 20. Summary of Rinsing Practices Used at Field Sites.**

	<b>Rinse Time (min:sec)</b>	<b>Rinse Tank Vol (l)</b>	<b>Rinse Flow Rate (l/min)</b>	<b>Rinse Water Source</b>	<b>Mixing<sup>1</sup></b>
Plant 1 ME Rinse 1	1:20	832	7.6	ME Rinse 2	1,2
Plant 1 ME Rinse 2	1:00	832	7.6	city	1,2
Plant 1 EC Rinse 1	2:10	832	7.6	EC Rinse 2	1,2
Plant 1 EC Rinse 2	1:00	832	7.6	city	1,2
Plant 1 AT Rinse 1	3:20	832	7.6	AT Rinse 2	1,2
Plant 1 AT Rinse 2	2:00	832	7.6	city	1,2
Plant 2 ME Rinse 1	2:05	415	3.8	city	1,2
Plant 2 EC Rinse 1	8:00	415	3.8	AT Rinse 1	1,2
Plant 2 AT Rinse 1	3:55	415	3.8	city	1,2
Plant 3 ME Rinse 1	1:15	892	9.8	H <sub>2</sub> SO <sub>4</sub> rinse	1,2
Plant 3 EC Rinse 1	2:00	892	7.6	EC Rinse 2	1,2
Plant 3 EC Rinse 2	4:20	892	7.6	AT Rinse 1	1,2
Plant 3 AT Rinse 1	6:04	892	7.6	city	1

<sup>1</sup> Mixing: 1 = Board Agitation; 2 = Aeration.

### Sample Collection

Samples were collected for analyses from the laboratory drag-out study tanks in the UT laboratory and from actual process baths and rinse tanks during the PWB industry site visits. For the laboratory drag-out study in the UT laboratory, grab samples were collected for surface tension and viscosity. The samples were collected directly from the experiment tank in a clean beaker, and the analyses were immediately performed.

Samples were collected during the PWB site visits from the microetch (ME), electroless copper (EC), and anti-tarnish (AT) process baths and their succeeding rinse tanks in the MHC process line. Grab samples were collected using either a plastic measuring cup or a sampling beaker, which consisted of a plastic beaker with a long handle attached. The sampling container was thoroughly rinsed with the sampling fluid prior to sample collection. The grab sample was then immediately transferred from the sampling cup or beaker into a clean 500 ml HPDE sample bottle and capped. Before the sampling event, pre-printed labels were prepared in duplicate, with one label pre-attached to the sample bottle. After the sample was collected, the remaining label was attached to the Sub-Unit Data Collection Log, and the sample description, person taking the sample, time of sample, sample volume, and method of preservation was recorded in ink. Duplicate samples taken in identical manner were collected at plants 1 and 2. At plant 3, the two samples were taken at different times in the board cycle. The first sample was taken just prior to the boards entering the rinse tank while the second was taken just after the boards were removed. Replicates were taken for approximately 20% of the samples. The sample bottles were sealed with color-coded tamper-proof tape (to identify the sampler and establish chain-of-custody), and placed in plastic lined containers for transport to the UT laboratory.

## Temperature

Temperature was measured *in-situ* in the laboratory drag-out tanks. In the field, temperature was measured on grab samples collected from the process and rinse tanks. Measurements were made immediately after collection.

## pH

pH was measured *in-situ* in the laboratory drag-out tanks. In the field, pH was measured on grab samples collected from the process and rinse tanks. Measurements were made immediately after collection.

### *Apparatus*

- Orion Digital Portable pH Meter, Model 250A.
- Orion Triode™ pH Electrode, Model 91-57BN.

### *Procedure for pH Measurements*

1. After the meter was calibrated, the electrode was placed into the laboratory drag-out tank or sample and agitated slightly.
2. When the pH display was stable, the pH was recorded on the Sub-Unit Data Collection Log.
3. The electrode was rinsed with deionized water, and the process repeated.

The pH meter was calibrated prior to taking measurements for each sub unit. A two buffer calibration was performed using the 4.01 and 7.00 buffers for the acid sub units, and 7.00 and 10.01 buffers for the alkaline sub units. The first measurement in a sub unit was made in the samples from the last rinse tank, and the measurements progressed up-line, with the last measurement made on the process bath sample.

## Conductivity

Conductivity measurements were performed both in the UT laboratory and at the PWB site visits. The instrument automatically compensates for temperature effects to a certain degree, except for acids. Since many of the PWB baths and rinses were acids, and temperature could have a significant effect on the conductance of these solutions, it was determined that all conductivity measurements should be made at the reference temperature of 25° C. The conductivity measurements originally made in the field at the PWB sites were re-analyzed on samples in the UT laboratory at a controlled temperature of approximately 25° C. At the beginning of each lab session, the conductivity meter was checked against a solution of known conductance to verify accuracy.

The conductivity measurements of the rinse tanks were within the meter range of 0.0 to 199.9 mS/cm; however, as anticipated, the values of some of the process baths were higher. Since conductivity is a nearly linear function of total dissolved solids (Snoeyink and Jenkins 1980), a 1:10 or 1:100 dilution with deionized water was performed on the sample if the initial reading was above the highest range on the meter. The measurement was then taken on the diluted sample, and the meter reading multiplied by the dilution factor.

Two temperature and conductivity readings were taken on each sample, with the mean values reported.

*Apparatus*

- Orion Conductivity/Temperature Meter, Model 122.

**Viscosity**

Viscosity was measured on site from grab samples collected from the rinse tanks, process baths, and laboratory drag-out tanks.

*Apparatus*

- Gilmont Falling Ball Viscometer, size 1, with stainless steel ball, range 1 to 10 centipoise.

*Procedure*

1. The temperature of the rinse tank or process bath was taken using the laboratory thermometer.
2. A grab sample was collected from the tank using a 2000 ml beaker. The viscometer, stainless steel ball, and thermometer were immediately submerged into the sample for approximately one minute to allow the laboratory equipment to equilibrate to the liquid temperature.
3. The inside of the viscometer was rinsed with the sample, then slowly filled with rinse or process bath liquid, making sure no air bubbles adhered to the sides of the viscometer.
4. The temperature of the liquid in the beaker was checked and compared with the tank temperature. In general, if the temperature difference was more than approximately 5°C, the beaker was emptied and a new sample collected.
5. The viscometer was held vertical in the center of the 2000 ml beaker. (The beaker still contained the rinse or process liquid, which acted as a temperature bath for the viscometer.) The stainless steel ball was carefully placed by hand into the filled viscometer, making sure no air bubbles stuck to the ball.
6. A stopwatch was used to time the descent of the ball between the fiducial lines on the viscometer. The time was recorded on the Sub-Unit Data Collection Log.
7. The viscometer and beaker were emptied, and the process repeated.

Using the mean descent time, the viscosity was calculated as follows:

$$m = K(r_f - r)t \quad \text{Eqn 17}$$

where:

- m = viscosity, centipoise
- K = viscometer constant (0.257 with stainless steel ball, based on laboratory calibration tests using deionized water and sucrose solutions, described below)
- r<sub>f</sub> = density of ball, mg/l (8.02 for stainless steel ball)
- r = density of liquid, mg/l
- t = time of descent, minutes

The viscosity was recorded on the Sub-Unit Data Collection Log.

The viscometer, stainless steel ball, and beaker were thoroughly rinsed with deionized water prior to the next test.

Before viscosity measurements were made in the field and on the laboratory drag-out tanks, a series of tests were performed to establish the viscometer constant, K, for the falling ball viscometer. The constant was obtained by measuring the time of descent of the stainless steel ball in standard solutions of known viscosity, and was calculated using the following relationship:

$$K = \frac{m}{(r_f - r)t} \quad \text{Eqn 18}$$

Three solutions were used in the investigation: 30 percent sucrose (by weight), 40 percent sucrose (by weight), and deionized water. Before the sucrose solutions were prepared, the sucrose was dried in a desiccator, and all glassware was cleaned and completely air dried. A 1000 ml volumetric flask was weighed on an electronic analytical balance, and the weight recorded to the nearest 0.01 gram. The appropriate amount of sucrose was weighed on the analytical balance (338.10 g and 470.60 g for the 30 percent and 40 percent solutions, respectively), and added to the clean, dry volumetric flask. Approximately 500 ml of deionized water was added to the flask, and the mixture agitated by swirling. Additional deionized water was added slowly, while being swirled, until the sucrose was completely dissolved and the bottom of the meniscus reached the 1000 ml reference line on the volumetric flask. The solution was allowed to rest to allow any entrapped air bubbles to rise. The volumetric flask containing the solution was weighed on the analytical balance, and the temperature was measured with a laboratory thermometer; both measurements were recorded in a laboratory research notebook.

The density of the sucrose solutions and the deionized water was calculated using the following relationship:

$$D = \frac{m}{v} \quad \text{Eqn 19}$$

where:

D = density, g/ml  
m = mass of solution = mass of flask and solution - mass of flask, g/L  
v = volume of solution, ml

Prior to the experiments to determine the viscometer constant, the sucrose solutions were gently stirred to ensure a homogeneous mixture. A laboratory thermometer was used to measure the temperatures of the sucrose solutions and deionized water, and the results were recorded in a laboratory research notebook. The same procedure as described above was used except the constant temperature bath was not needed because the experiments were done at ambient temperature. Instead, the filled viscometer was held vertical in a 50 ml glass cylinder. The viscometer constant, K, was determined to be 0.257 by fitting equation 17 to the experimental time and literature values of viscosity.

## Specific Gravity

Specific gravity was measured *in-situ* in the laboratory drag-out tanks. In the field, specific gravity was measured on grab samples collected from the process and rinse tanks. Measurements were made immediately after collection.

### *Apparatus*

- Hydrometer, Fisherbrand, range 0.890 to 1.000.
- Hydrometer, Fisherbrand, range 1.000 to 1.600.
- 500 ml glass cylinder (optional).

Before the hydrometers were used for measurements for the rinse tanks, process baths and laboratory drag-out tests, the accuracy of the instruments was verified. Hydrometer readings were taken on deionized water and a 40 percent (by weight) sucrose solution. The temperature of the water and sucrose solution was measured with a laboratory thermometer, and the specific gravity measurements were compared with published values. Results of the verification for deionized water resulted in a value 0.15% higher than the expected published value of 1.000 at 20° C, and 0.5% less than the published value of 1.176 for the 40 percent sucrose solution at 20° C.

## Surface Tension

Surface tension was measured in the UT laboratory on grab samples collected from the rinse tanks, process baths, and laboratory drag-out tanks.

### *Apparatus*

- Fisher Surface Tensiomat, Model 21, with platinum-iridium ring.
- 5 cm inch diameter glass vessel, approximately 1.3 cm deep.
- Magna-Whirl water bath.

### *Procedure*

1. A water bath was prepared to simulate the temperature of the rinse tank or process bath as measured in the field and recorded on the Sub-Unit Data Collection Log.
2. The rinse tank or process bath sample bottles were placed in the water bath, and allowed to equilibrate to the bath temperature. The water bath and sample temperatures were intermittently monitored using the thermometer. The sample bottles remained in the water bath until used for the surface tension measurement.
3. The clean platinum-iridium ring was placed on the hook on the lever arm of the tensiostat.
4. A clean 5 cm diameter glass vessel was filled with a portion of the sample (transferred immediately from the water bath) and placed on the sample table inside the tensiostat.
5. The sample table was raised until the ring was immersed in the liquid to a depth of approximately 3 mm.
6. The torsion arm on the tensiostat was released, and the instrument was adjusted to a zero reading by turning the knob on the right side of the case until the index and its image were in line with the mark on the mirror. Care was taken to ensure the ring remained in the liquid by adjusting the height of the sample table. The knob on the front of the case beneath the main dial was adjusted until the vernier read zero on the outer scale of the dial.

7. The sample table was lowered until the ring was at the surface of the liquid. At the same time, the knob on the right side of the case was adjusted to keep the index in line with the mark on the mirror. The two simultaneous adjustments were continued until the distended film at the surface of the liquid broke.
8. The reading on the scale at the breaking point (surface tension in dynes per centimeter) was recorded on the Sub-Unit Data Collection Log.
9. The liquid was emptied from the glass vessel, and the process was repeated.
10. Both the platinum-iridium ring and glass vessel were rinsed with deionized water prior to the next test.

Prior to the surface tension tests, the calibration of the tensiostat was checked and the platinum-iridium ring was thoroughly cleaned.

To verify the calibration according to the instrument's instruction manual, the ring was placed on the lever arm and the instrument was adjusted to a zero reading. A 600 mg piece of aluminum foil was placed on the ring, and the knob on the right side of the case was adjusted until the index and its image were in line with the mark on the mirror. The dial reading was recorded, and compared with the calculated surface tension:

$$S = \frac{Mg}{2L} \qquad \text{Eqn 20}$$

where:

- |   |   |   |
|---|---|---|
| S | = | dial reading = apparent surface tension in dynes/cm |
| M | = | weight (0.6 grams)                                  |
| g | = | acceleration of gravity (980 cm/sec <sup>2</sup> )  |
| L | = | mean circumference of ring (6.00 cm)                |

The platinum-iridium ring was cleaned per the manufacturer's instructions: the ring was: 1) soaked in concentrated nitric acid for approximately 2 minutes, then rinsed with deionized water; 2) rinsed with acetone, followed by deionized water; and 3) flamed with a Bunsen burner.

Before surface tension measurements were made, the surface tension of deionized water was checked at 20°C to verify accuracy. Seven measurements were made, with a mean value of 74.96 dynes/cm, a standard deviation of 2.03 dynes/cm. This mean value is 4.2 percent higher than the expected value of 72 dynes/cm for the deionized water.

### Metals Analysis

Sodium and/or Potassium analyses were conducted in the UT laboratory on grab samples collected from the process baths and rinse tanks.

#### *Apparatus*

- Allied Analytical Systems Atomic Absorption Spectrophotometer, IL Video 12, Serial Number 1857.
- Sartorius Analytical Balance, Model AC 120S, UT ID Number 427286.

### *Reagents*

- Sodium calibration standard, Fisher Scientific, 1000 mg/L.
- Potassium calibration standard, Fisher Scientific, 1000 mg/L.
- Potassium chloride (KCl), Fisher Scientific, certified grade.
- Lanthanum chloride (LaCl 6H<sub>2</sub>O), Fisher Scientific, certified grade.

### *Procedure*

1. Stock potassium chloride solution was prepared by dissolving 23.84 g. of potassium chloride in 250 ml of deionized water in a volumetric flask. This produced a solution of 50,000 mg/L as K, which was used as an ionization suppressant for the sodium samples. A stock solution of lanthanum chloride was prepared by dissolving 12.72 g. of lanthanum chloride in 100 ml of deionized water in a volumetric flask. This produced a solution of 50,000 mg/L as La, which was used as an ionization suppressant for the potassium samples.
2. Sodium and potassium standards were prepared by diluting the Fisher Scientific calibration standards with deionized water to achieve the desired standards concentrations.
3. The samples were prepared by performing dilutions with deionized water to get the anticipated analyte concentrations within the linear range of the instrument. Volumetric pipettes and volumetric flasks were used, and the samples were transferred to new, clean 125 ml HDPE sample bottles. Samples were acidified with ultrapure nitric acid, and ionization suppressants were added to achieve a concentration of 2000 mg/L as K for the sodium samples, and 1000 mg/L as La for the potassium samples.
4. The appropriate lamp was inserted in the atomic absorption spectrophotometer, and a safety check of all settings was performed. The instrument electronics were turned on and allowed to warm up for approximately 30 minutes.
5. The instrument printer, compressed air, and acetylene were turned on. The pilot was lit, the flame adjusted, and the sampling tube was placed in a fresh beaker of deionized water.
6. The instrument was calibrated with the appropriate sodium or potassium standards. A standards curve was printed, and a linear regression performed to check linearity of the curve. If the value of  $r^2$  value was below 0.9950, the instrument was re-calibrated with fresh standards.
7. The prepared samples were analyzed, beginning with the rinse samples and progressing up-line to the process tank. Approximately ten analyses were run per sample, each lasting approximately eight seconds. Results were printed and transferred to an Excel spreadsheet.
8. The method of standard additions was performed on process bath samples to reduce matrix effects. The samples were diluted 1:1 with known standards and analyzed in the absorption mode. Generally, 0, 50, 100 and 200 mg/L standards were used for potassium analyses, and 0, 20, 50 and 100 mg/L standards were used for sodium analyses; however there was some variation since it was necessary to keep concentrations within the instrument's linear range. A plot of absorption verses concentration of added standards was then prepared, from which the actual concentration in the sample was derived. If necessary, standard additions were performed on the succeeding rinse tanks, as described later in this section.

Before and during the atomic absorption analyses, all laboratory glassware and sample bottles were acid washed in accordance with Standard Methods.

The analyte (sodium or potassium) was determined based on process bath composition, as provided by either industry representatives, manufacturers' material safety data sheets, or previous research conducted by the University of Tennessee's CCPCT.

Because of the extremely high anticipated concentration of analyte in some of the process baths, along with the wide range of anticipated concentrations between the process baths and rinse tanks, atomic absorption analyses were conducted using the least sensitive wavelengths (330.2 nm for sodium, and 404.4 nm for potassium) whenever possible. Dilutions were still necessary on many of the samples. For sodium samples with very low sodium concentrations, it was necessary to use the most sensitive wavelength of 589.0 nm.

The instrument was calibrated at the beginning of each lab session by using generally five calibration standards within the linear range of the instrument, including a zero standard. The standards used for the least sensitive wavelength for sodium (330.2 nm) were usually 0, 20, 50, 100, and 150 mg/L; however these occasionally varied depending on the anticipated concentration of the sample. In all cases, the standards were chosen to best bracket the sample concentration. Standards used for the most sensitive sodium analyses (589.0 nm wavelength) were usually 0, 0.25, 0.50, 0.75, 1.0 and 1.25 mg/L. Calibration standards for the least sensitive wavelength for potassium (404.4 nm) were usually 0, 50, 100, 200 and 600. As with the sodium analyses, standards were chosen to best bracket the sample potassium concentration. Standards checks were performed during the measurements to ensure the instrument had not drifted. The checks usually were performed after every four or five measurements, but always after ten measurements were taken.

The samples were prepared for analysis by dilution with deionized water to achieve an anticipated analyte concentration within the linear range of the instrument. The anticipated concentrations were based on previous research conducted by the University of Tennessee's CCPCT. Alkali salts were added to the samples and standards as an ionization suppressant. Potassium chloride was added to sodium samples at 2000 mg/L, and lanthanum chloride at 1000 mg/L was added to the potassium samples. Process and rinse tank samples and standard solutions were acidified to  $\text{pH} < 2$  in accordance with Standard Methods, using ultrapure concentrated nitric acid. Electroless copper samples were not acidified due to the possibility of the baths containing cyanide.

As an interference check, a standard additions analysis was performed on one sample for each process bath, and compared with analysis results performed without standard additions. Whenever there was a difference greater than 10 percent between the two measurements, a standard addition analysis was performed on the duplicate bath sample, and the standard addition results were used. If standard additions were necessary for the process bath samples, the succeeding rinse tank samples were also checked, to determine if standard additions should be used.

## **Quality Assurance and Quality Control (QA/QC)**

Prior to the site visit to collect the samples, the 500 ml new HDPE sample bottles were thoroughly cleaned with detergent, triple rinsed with deionized water, and allowed to air dry. Field blanks were used to monitor any contamination from the bottles. The field blanks were pre-labeled and filled with deionized water in the UT laboratory prior to the site visits. During the visit, the bottles were opened for approximately two minutes, then re-sealed.

All laboratory equipment transported to the site was thoroughly cleaned according to Standard Methods prior to leaving the UT laboratory, and was again thoroughly cleaned between sites. All laboratory equipment, including reagents and deionized water was transported from the UT laboratory, including cleaning supplied. The samples remained in the custody of the sampling team until arrival back to the UT laboratory, where they were placed in a limited access, locked cold room until analyses.

## **Results from Analysis of Field Samples**

Mean values of temperature, specific gravity, viscosity, conductivity, surface tension for each of the field samples are summarized in Table 21.

Measurements of conductivity, specific gravity, surface tension, viscosity were all completed in duplicate. The coefficients for all measurements were all excellent (conductivity 0.04, surface tension 0.005, specific gravity 0.001% and viscosity 0.073).

Sodium and potassium concentrations are summarized in Table 22. Replicate samples at plants 1 and 2 were taken in identical manner, and the results were averaged and reported as a single value. At plant 3, two samples were taken at different times in the board cycle time. Samples labeled "A" were taken just prior to the boards entering the rinse tank and should normally correspond to the lowest concentration present in the rinse tank. Samples "B" and "R" were taken just after the boards were removed from the rinse tank and should be near the maximum concentration in the rinse cycle. The individual samples from plant 3 were not averaged, but reported individually. Details of the analytical procedure used for each sample are summarized in the Appendix.

**Table 21. Temperature, Specific Gravity, Viscosity, Conductivity, Surface Tension for Field Samples.**

Sample Name	Temp., °C	Specific Gravity	Viscosity, cP	Conductivity, mS/cm, 25 °C	Surface Tension, dynes/cm
Plant 1 ME Process	30	1.110	1.140	304,000	76.2
Plant 1 ME Rinse 1	20	1.005	1.112	1,935	75.9
Plant 1 ME Rinse 2	20	1.004	1.142	213	75.6
Plant 1 EC Process	45.5	1.170	1.218	224,000	73.2
Plant 1 EC Rinse 1	21	1.003	.977	1,043	76.0
Plant 1 EC Rinse 2	20	1.005	1.097	224	76.3
Plant 1 AT Process	19	1.004	1.172	341	72.2
Plant 1 AT Rinse 1	20	1.002	1.097	229	74.4
Plant AT Rinse 2	20	1.002	1.022	223	76.2
Plant 1 FB	NA	NA	NA	1.8	76.2
Plant 2 ME Process	37	1.175	1.246	477,000	78.0
Plant 2 ME Rinse 1	15	1.004	1.172	2,170	77.0
Plant 2 EC Process	38	1.110	1.421	119,600	51.2
Plant 2 EC Rinse 1	20	1.002	.932	676	73.2
Plant 2 AT Process	19	1.005	1.202	353	75.0
Plant 2 AT Rinse	16.5	1.005	1.037	256	76.3
Plant 2 FB	NA	NA	NA	1.9	76.1
Plant 3 ME Process	29	1.145	1.340	168,400	77.6
Plant EC Process	54	1.115	1.139	261,000	56.2
Plant 3 EC Rinse 1	27	1.002	0.992	736	74.0
Plant 3 EC Rinse 2	30	1.003	NA	155	75.4
Plant 3 AT Process	25	1.005	1.127	543	72.2
Plant 3 AT Rinse	30.5	0.994	0.798	156	73.6
Plant 3 FB	NA	NA	NA	1.8	75.0

**Table 22. Metals Concentrations Measured in Field Samples.**

Sample Name	Sodium, mg/L	Potassium, mg/L	Method
Plant 1 ME Process		20,380	Standard Additions
Plant 1 ME Rinse 1		77.4	Standard Curve
Plant 1 ME Rinse 2		<7.5	Standard Curve
Plant 1 EC Process	67,750		Standard Additions
Plant 1 EC Rinse 1	242		Standard Curve
Plant 1 EC Rinse 2	24.5		Standard Curve

Sample Name	Sodium, mg/L	Potassium, mg/L	Method
Plant 1 AT Process	2.8	94	Standard Additions
Plant 1 AT Rinse 1		<7.5	Standard Curve
Plant 1 AT Rinse 2		<7.5	Standard Curve
Plant 1 Makeup water	20.15	<7.5	Standard Curve
Plant 1 FB		<7.5	Standard Curve
Plant 2 ME Process		62,300	Standard Additions
Plant 2 ME Rinse 1		98.8	Standard Curve
Plant 2 EC Process	63,450		Standard Additions
Plant 2 EC Rinse 1	128.6		Standard Curve
Plant 2 AT Process	30.8	<7.5	Standard Additions
Plant 2 AT Rinse	34.5	<7.5	Standard Curve
Plant 2 Makeup water	31.36	<7.5	Standard Curve
Plant 2 FB	<0.01		Standard Curve
Plant 3 ME Process	41,550		Standard Additions
Plant 3 ME Rinse 1-A	173.6		Standard Additions
Plant 3 ME Rinse 1-B	242		Standard Additions
Plant 3 ME Rinse 1-R	289		Standard Additions
Plant 3 EC Process	72,950		Standard Additions
Plant 3 EC Rinse 1-A	109.3		Standard Curve
Plant 3 EC Rinse 1-B	173.5		Standard Additions
Plant 3 EC Rinse 1-R	191.7		Standard Curve
Sample Name	Sodium, mg/L	Potassium, mg/L	Method
Plant 3 EC Rinse 2-A	24.3		Standard Curve
Plant 3 EC Rinse 2-B	24.4		Standard Curve
Plant 3 AT Process	111		Standard Additions
Plant 3 AT Rinse 1-A	19.1		Standard Curve
Plant 3 AT Rinse 1-B	19.1		Standard Curve
Plant 3 AT Rinse 1-R	23.2		Standard Curve
Plant 2 Makeup water	23.1	<7.5	Standard Curve
Plant 3 FB	<0.1		Standard Curve

The pooled instrumental relative standard deviation for potassium was determined to be 0.77%, based on eighteen potassium samples with a mean sample concentration of 113.6 mg/L, and a pooled instrumental standard deviation of 0.87 mg/L. The pooled instrumental relative standard deviation for sodium was determined to be 1.6% based on seventy-three analyses with a mean concentration of 60.6 mg/L. The pooled instrumental standard deviation was 0.97 mg/L. Data on which these calculations are based are included in the Appendix.

The relative standard deviation for duplicate potassium samples ranged from 0.17 to 6.95% for tests run with no standard additions, with a pooled standard deviation of 3.46 mg/L. There were no duplicate or replicate analyses for potassium using the method of standard additions. The relative standard deviation for duplicate sodium measurements without standard additions ranged from 0.11 percent to 18.94 percent, with a pooled standard deviation of 8.05 mg/L. The relative standard deviation for duplicate sodium analyses performed with standard additions ranged from 0.52 to 6.13%, with a pooled standard deviation of 2.76 mg/L. Data for duplicate samples from which these results were determined are listed in the Appendix.

## DYNAMIC MASS BALANCE MODEL FOR INTERPRETATION OF FIELD DATA

The field data collected at the PWB manufacturers was used to validate the drag-out component of the wastewater generation model. The output from the model is the *average* mass rate of contaminant in the rinse water from a particular process bath; the model can also calculate average concentrations in the rinse tank effluent by dividing by the rinse flow rate.

However, the average concentration predicted by the model does not correspond directly to the contaminant concentrations measured in the field samples. The MHC process is dynamic in that the concentrations of contaminants in the rinse effluent change as a function of time. The operation cycle of a given rinse tank consists of a short period of time in which a board is immersed in the tank, followed by a longer period of time during which no boards are in the tanks. Contaminants are continually flushed from the rinse tank during the entire operation time of the bath. As a result of this operational practice, the rinse-tank concentration history will be a periodic saw-tooth wave function. In the field, *instantaneous grab* samples were collected from the rinse tanks, usually immediately after removal of the board. Clearly, the concentrations in the instantaneous grab samples may not be directly comparable to the average concentration calculated by the model; therefore, a means of verifying the model is needed. A dynamic material balance model was used to compare the concentration of contaminant in the grab samples with the average concentration of contaminant predicted by the models.

The following material balance equation describes the concentration of contaminant in a completely-mixed rinse tank:

$$QC_o - QC = V \frac{dC}{dt} \quad \text{Eqn 21}$$

where:

Q	=	flow rate through the tank, L <sup>3</sup> /t
V	=	tank volume, L <sup>3</sup>
C	=	concentration of contaminant in the tank, M/L <sup>3</sup>
C <sub>o</sub>	=	concentration of contaminant in the feed water to the tank, M/L <sup>3</sup>
t	=	time, t

The concentration of contaminant in the tank as a function of time can be determined by separating the variables in equation 21 and integrating using appropriate boundary conditions. Assume that when the line is first started (before the first board is dipped in the tank) that the contaminant concentration in the tank is equal to the feed water concentration. Also assume that at t=0 a rack of boards, containing mass of contaminant M, instantly releases all of its contaminant to solution. Under these conditions, the concentration in the tank at t=0 is:

$$C = C_o + \frac{M}{V} \quad \text{Eqn 22}$$

The solution to equation 21 describing the concentration history after removal of the first board is then given by:

$$\int_0^t \frac{Q}{V} dt = \int_{M/V+C_o}^C \frac{dC}{C_o - C} \quad \text{Eqn 23}$$

$$C = C_o + \frac{M}{V} \exp\left(-\frac{Qt}{V}\right) \quad \text{Eqn 24}$$

As time progresses additional boards will enter the rinse tank. Assume that additional boards enter the tank at a constant period of  $l$ . It is convenient to redefine  $t$  as:

$$t = n l + q \quad \text{Eqn 25}$$

where

$n$  = number of cycles completed since  $t = 0$

$q$  = time elapsed in the current cycle,  $t$

The effluent history during the rinsing cycle for the second board processed after start-up would be given by:

$$\int_0^q \frac{Q}{V} dq = \int_{(M/V)[1+\exp(-Ql/V)]+C_o}^C \frac{dC}{C_o - C} \quad \text{Eqn 26}$$

$$C = C_o + \frac{M}{V} \exp\left(-\frac{Qq}{V}\right) + \frac{M}{V} \exp\left(-\frac{Q(l+q)}{V}\right) \quad \text{Eqn 27}$$

This result can be extended to represent the effluent history for the rinsing period after the  $n^{\text{th}}$  board is rinsed:

$$C = C_o + \frac{M}{V} \exp\left(-\frac{Qq}{V}\right) \sum_{k=0}^n \exp\left(-\frac{kQl}{V}\right) \quad \text{Eqn 28}$$

Steady-state is defined to occur when  $n = \infty$ . Substituting

$$\sum_{k=0}^{\infty} \exp\left(-\frac{kQI}{V}\right) = \frac{1}{1 - \exp\left(-\frac{QI}{V}\right)} \quad \text{Eqn 29}$$

yields an expression concentration history for a single rinse tank, operating at steady-state:

$$C = C_o + \frac{M}{V} \exp\left(-\frac{Qq}{V}\right) \frac{1}{1 - \exp\left(-\frac{QI}{V}\right)} \text{ for } q < I. \quad \text{Eqn 30}$$

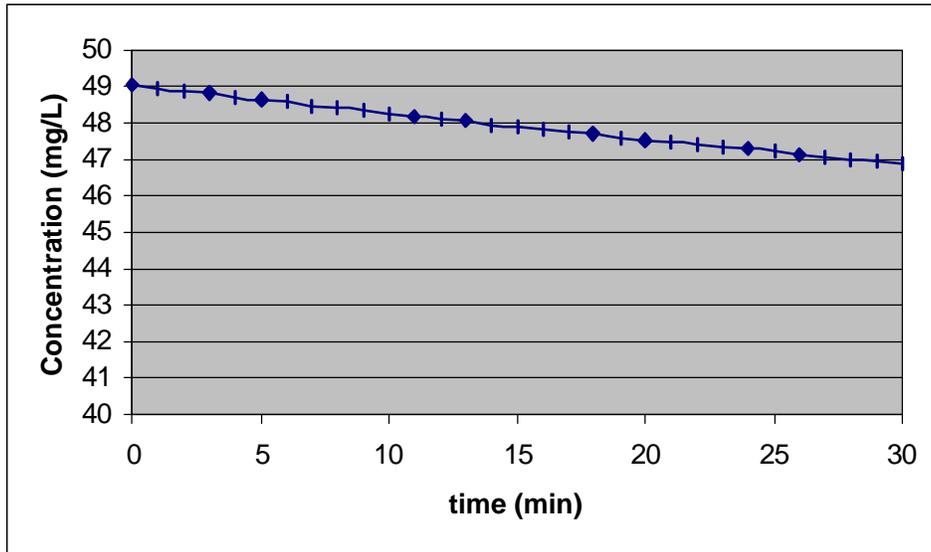
*Example:*

A rinsing tank receives a rack containing 60 ft<sup>2</sup> of boards every 30 minutes. The drag-out rate is 10 mL/ft<sup>2</sup> and the contaminant concentration in the process tank is 3000 mg/L. The rinse rate is 2 gpm and the tank is 220 gallons in volume. The feed water contains 40 mg/L of the contaminant. Calculate the effluent concentration history during the 30 minute cycle period under steady-state conditions:

$$\frac{M}{V} = 60 \text{ft}^2 \left( \frac{10 \text{mL}}{\text{ft}^2} \right) \left( \frac{3000 \text{g}}{\text{L}} \right) \left( \frac{\text{L}}{1000 \text{mL}} \right) \left( \frac{1}{220 \text{gal}} \right) \left( \frac{\text{gal}}{3.78 \text{L}} \right) = 21.6 \text{mg/L} \quad \text{Eqn 31}$$

$$C = 40 + 2.16 \exp\left(-\frac{2q}{220}\right) \frac{1}{1 - \exp\left(-\frac{-2 \cdot 30}{220}\right)} \quad \text{Eqn 32}$$

Equation 32 is plotted over the course of one process cycle in Figure 6.



**Figure 6. Example Concentration History of Rinse Tank Effluent During One Plating Cycle.**

## MODEL VALIDATION

The purpose of the field samples was to validate the drag-out prediction model and the overall mass balance approach to predicting wastewater quality from PWB facilities. The dynamic material balance model for the rinsing process was developed in the previous section to facilitate this comparison. First, equation 30 was solved for the mass of contaminant in the drag-out:

$$M = (C - C_0)V \exp\left(\frac{Qq}{V}\right) \left[1 - \exp\left(\frac{-QI}{V}\right)\right] \quad \text{Eqn 33}$$

The volume of the drag-out could then be calculated by dividing the mass of contaminant in the drag-out by the bath concentration:

$$V_{\text{drag-out}} = \frac{M}{C_{\text{bath}}} \quad \text{Eqn 34}$$

The drag-out volumes calculated from the field data and the dynamic mass balance (equations 33 and 34) are compared to those predicted using the drag-out regression model (equation 15) in Table 23. Replicate samples at the plants 1 and 2 were taken in identical manner, and the results were averaged and reported as a single value. At plant 3, the duplicate samples were taken at different times in the board cycle time. Samples labeled “A” were taken just prior to the boards entering the rinse tank and should normally correspond to the lowest concentration present in the rinse tank. Samples “B” and “R” were taken just after the boards were removed from the rinse tank and should be near the maximum concentration in the rinse cycle. Samples 3MER1-A and -B were taken soon after the MHC line had been shut down for a short period of time and may have been erroneously low. The individual samples from plant 3 were not averaged; separate calculations were made for each one. Sodium and potassium concentrations in the anti-tarnish rinse tanks were too low to accurately calculate either the mass of contaminant in the drag-out or the drag-out volume.

The drag-out volumes calculated from the field data are consistently less than those predicted by the drag-out model. They are also significantly less than those measured both in the laboratory experiments performed as a part of this work and the data collected by Pagel (1992). For example, the drag-out volumes from Microetch baths calculated from our field data ranged from 22.8 to 53.6 mL/m<sup>2</sup>, compared to a range of 76 to 122 mL/m<sup>2</sup> in this study and a range of 57 to 145 mL/m<sup>2</sup> in Pagel’s work. Similarly, the drag-out volumes from the Electroless baths calculated from our field data ranged from 9.73 to 32.9 mL/m<sup>2</sup>, compared to a range of 20.4 to 81.8 mL/m<sup>2</sup> in Pagel’s work. A possible explanation is that the drag-out volumes calculated from the field data were based on the assumption in the dynamic mass balance model that all the contaminant was released instantaneously from the PWB and that the rinse tank was perfectly mixed. The rinsing tanks used in PWB plants may not approximate this ideal behavior. Rinse water typically enters the bottom of the rinse tank and flows over a weir at the water surface. As the board enters the tank, it is likely that a significant fraction of the pollutant flows over the weir prior to being mixed

throughout the tank. Fluid shear may contribute to the loss of contaminant near the water surface of the tank as the board enters the tank. The grab samples were generally collected immediately following removal of the board from the rinse tank. We hypothesize that the short-circuiting process described above may have caused a large fraction of the contaminant to be removed from the rinse tank prior to the time that we collected the sample. Our laboratory drag-out study, and the work of Pagel (in which the rinse water flow rate was set to zero during the sampling) were not subject to this influence.

**Table 23. Comparison of Drag-Out Volumes Calculated from Field Samples to Those Predicted by Regression Model.**

Sample Description	Drag-Out Volume Calculated from Field Data, mL/m <sup>2</sup>	Drag-Out Volume Calculated from Regression Model, mL/m <sup>2</sup>
Plant 1, Microetch	53.6	127
Plant 1, Electroless Copper	32.9	59.1
Plant 2, Microetch	22.8	102
Plant 2, Electroless Copper	23.2	39.9
Plant 3, Microetch A	28.2	98.2
Plant 3, Microetch B	41.0	98.2
Plant 3, Microetch R	37.9	98.2
Plant 3, Electroless A	9.73	34.7
Plant 3, Electroless B	6.83	34.7
Plant 3, Electroless R	10.9	34.7

A regression equation was fitted to the data in Table 23, resulting in the following relationship ( $r^2 = 0.71$ ):

$$V_{field} = 0.36V_{predicted} + 0.68 \quad \text{Eqn 35}$$

where:

$V_{field}$  = drag-out volume calculated from the field data  
 $V_{predicted}$  = is the drag-out volume predicted by the regression model

The slope of the regression equation suggests that about 2/3 of the total mass of contaminant flows over the weir prior to being mixed. The relatively good correlation coefficient indicates that the field and predicted drag-out volumes were comparative on a relative basis. This suggests that the drag-out regression model and overall mass balance approach may be valid for making relative comparisons between process alternatives.

## CONCLUSIONS AND RECOMMENDATIONS FOR FUTURE WORK

### Conclusions

- Contaminant mass in PWB process wastewaters can be expressed as a mass balance in which the mass of contaminant in the wastewater is equal to the mass of contaminant released via drag-out from the process baths (which ultimately ends up in the rinse tanks), periodic dumping of process tanks into the wastewater, and stripping deposits from racks. Drag-out is generally considered to be the major contaminant source. Data quantifying composition of the process baths, the volume of wastewater produced, and the frequency of bath dumps are usually collected during the course of the DFE process. For example, this information was collected for the MHC process during a previous study by the University of Tennessee CCPCT (Kincaid et al. 1997).
- Very little data exists quantifying the rate of drag-out from PWB processes, i.e., the mass or volume of drag-out per unit surface area of PWB, e.g., mL/m<sup>2</sup>. A study reported by Pagel at Micom, Inc. is the only readily available study on PWB facilities. Limited drag-out research has been conducted on flat pieces, most notably by Süß. However, the numerous small holes present in PWBs renders application of drag-out volumes measured from non-PWB pieces problematic. Practitioners tend to use rules-of-thumb or historically accepted values for drag-out. This one-size-fits-all approach ignores process specific information such as bath type, viscosity, surface tension, board withdrawal rate, or drain time. Drag-out rates reported in the literature for vertically-oriented flat pieces range from 10 to 160 mL/m<sup>2</sup>.
- Commonly-cited equation found in the literature offer predictions of the drag-out rate as a function of kinematic viscosity and board withdrawal rate. Süß showed that this equation does not predict drag-out very well for the rectangular flat pieces that he studied. There was no relationship between kinematic viscosity and drag-out, and two previously proposed predictive equations performed poorly.
- Several variables have been shown to affect the drag-out rate. Studies at Micom, Inc. reported by Pagel (1992) showed the importance of longer drainage time and slower withdrawal rate in reducing drag-out. Süß (1990, 1992) also found that these variables are important as well as the angle of the board during drainage. No research was found that addressed the effect of surface tension. Based on the present study, surface tension may be an important variable.
- Considerable literature exists on rinsing theory which appears highly developed and well studied for ideal mixing situations. While rinsing theory is not as well developed for non-ideal mixing, previous researchers have concluded the assumption of ideal mixing is valid for estimating long-term-average wastewater concentrations because nearly all of the drag-out ultimately reaches the wastewater effluent.
- Laboratory studies conducted as part of this research expanded the data base of drag-out rates for two PWB process baths and several operating conditions. The experimental procedures showed good reproducibility, and the data were consistent with previous research.

- A regression model for predicting drag-out volume was developed using the available data bases of Süß (1990, 1992), Pagel (1992), and the present study. The dependent variables were a choice of two types of process baths (plus a default for any other type of bath), board withdrawal rate, drain time, board size, and presence of drilled holes. The model had an  $R^2$  of 0.852.
- The regression model for predicting drag-out rate was incorporated in a computer model for predicting contaminant mass loading and mean pollutant concentrations from PWB manufacturing process lines. The model was written as a Visual Basic macro within an EXCEL spreadsheet. Input variables included facility production rate, board size, number and types of process baths, bath composition, frequency of bath dumps, and wastewater production rate.
- Samples were collected from three PWB facilities in order to validate the drag-out model. Samples were collected from various process and rinse tanks and analyzed for temperature, specific gravity, viscosity, surface tension, conductivity, and potassium or sodium concentration. Since it was not convenient to collect composite samples from the rinse tanks, grab samples were collected at various times after a board was inserted into a rinse tank. An equation was developed to relate the time-dependent concentration of potassium or sodium in the rinse tank to the drag-out volume. Unfortunately, it appears that poor mixing in the rinse tanks led to unrepresentative sampling. Although the apparent drag-out rates were about 1/3 of the predicted rates, a comparison of drag-out rates between process tanks showed a correlation ( $r^2 = 0.71$ ) with the previously developed regression model, and in that sense lend support to it.

## Recommendations

- The authors believe that this work has resulted in a more universally applicable method for estimating the mass and concentration of contaminants in a PWB process wastewater than currently exists, especially for relative evaluations. However, much can still be done to improve the model since the existing data are so limited. Previous work has not studied the effect of surface tension, but the laboratory studies in this work showed that surface tension may be an important variable. Indeed, one of the drag-out reduction best practices is to use a wetting agent which would reduce surface tension. The effect of viscosity was previously thought to be important, but neither Süß nor this work found it to be significant. There has also been only one previously reported study of an actual PWB facility. The authors believe that a better quantitative understanding of the variables affecting drag-out could lead to the development of a better prediction equation. The first phase of such research should focus determining the effect of bath fluid properties and operating variables under controlled laboratory conditions. Expansion and testing of the model could be accomplished by samples collected at PWB facilities during a second phase of the study.
- Beyond determining the wastewater quality emanating from PWB manufacturing processes, there is a need to assess the fate of the chemicals in the PWB wastewater both in the onsite treatment processes at PWB manufacturing facilities and at Publicly-Owned Treatment Works (POTW). Information of the effect of chemical speciation on the fate of

pollutants is especially needed. For example, metals are one of the primary pollutants of concern in PWB wastewater, and it is likely that many of the metals are chemically complexed in PWB wastewater. On-site treatment processes are likely to preferentially remove the least stable metal complexes, while the most stable complexes are discharged to the POTW. Standard removal efficiencies for metals in activated sludge processes are probably not applicable to these highly complexed metals and the potential for release of the metals to the aquatic environment may be underestimated.

- A third issue needful of better understanding is the volatilization of chemicals from tanks and baths such as in PWB plating processes and other manufacturing processes. The volatilization models used in the previous assessment of emissions for the MHC process and the present assessment of surface finishing assume gas-side control of the mass transfer, i.e., volatilization, of chemicals from the process baths. In the MHC, and presumably in the surface finishing process, there were several chemicals whose mass transfer appeared to be liquid-side controlled. The mass transfer model used does not apply for this situation and could lead to an overestimate of the emission and consequent risk for these chemicals. It would be productive to research the literature to find more appropriate liquid-side control mass transfer models and applicable constants for various types of manufacturing process tanks. For example, there is a body of literature available on surface renewal theory models which would be more appropriate for liquid-side mass transfer control. This literature search could be completed within a year and a decision made at that time as to whether any lab based research is warranted.

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## LIST OF SYMBOLS

A	=	area of the sheet
$c_i$	=	mass content of the component is kg of component per kg of solution
$C_o$	=	concentration of contaminant solution being drug into rinse tank
$C_r$	=	concentration of contaminant in the effluent of the $r^{\text{th}}$ rinse tank
$C_t$	=	concentration of contaminant in rinse tank after t min
D	=	volume of drag-over or drag-out on rack and work rinsing operation
$D_i$	=	coefficient calculated as shown below for each component for use in the method given by Zaytsev and Aseyev
$d_{0i}, d_{1i}, d_{2i}$	=	empirical coefficients chosen for each electrolyte component from a table for use in the method given by Zaytsev and Aseyev
f	=	film thickness, cm
$f_{dr}$	=	thickness of the film that drains off the sheet
$F_{dr}$	=	function describing a relationship between the independent variables and thickness of the film that drains from the sheet
g	=	gravity (981 cm/s <sup>2</sup> )
h	=	height of metal sheet
K	=	unknown constant determined by experiments
m	=	unknown exponent determined by experiments
n	=	number of rinsing operations in t min
Q	=	rate of fresh water flow
r	=	number of rinse tanks in series
t	=	time interval between rinsing operations
T	=	temperature of solution, °C
$t_{dr}$	=	drainage time, s
$t_w$	=	withdrawal time, s
V	=	velocity of withdrawal
$v_A$	=	withdrawal rate of metal sheet, cm/s
$V_t$	=	volume of rinse tank
$\bar{V}$	=	volume of liquid that drains from the rectangular sheet
$\nu$	=	kinematic viscosity, cm <sup>2</sup> /s
$\rho$	=	density of electrolyte, gm/cm <sup>3</sup>
$\mu$	=	dynamic viscosity of electrolyte, g/(cm·s)
$\mu_o$	=	viscosity of water, Pa·s
$\sigma_{dr}$	=	surface tension of the liquid